Supporting Information
Higher-Order Cyclopropenimine Superbases. Direct Neutral Brønsted Base Catalyzed Michael Reactions with α-Aryl Esters.

Eric D. Nacsa and Tristan H. Lambert*

Department of Chemistry, Columbia University, New York, NY 10027

Table of Contents

General Information.

All reactions were performed using oven- or flame-dried glassware under an atmosphere of dry argon with magnetic stirring, unless otherwise noted. Non-aqueous reagents were transferred by syringe under argon. Organic solutions were concentrated using a Buchi rotary evaporator. Methylene chloride, benzene, toluene, THF, and diethyl ether were dried using a J.C. Meyer solvent purification system. Triethylamine and diisopropylamine were distilled from CaH_2 under argon. Quinoline was distilled from zinc dust under vacuum. Phosphorus pentachloride was purified by sublimation under vacuum at 180-200 °C and stored in a glove box. All other solvents and commercial reagents were used as provided unless otherwise noted. Flash column chromatography was performed employing 32-63 μm silica gel (Dynamic Adsorbents Inc). Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (SiliCycle).

^{1}H and ^{13}C NMR were recorded on Bruker DRX spectrometers in deuterated solvents and at frequencies as noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ, in ppm), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, quint=quintet, hex=hextet, hept=heptet, m=multiplet, br=broad, app=apparent), coupling constant (*J*, in Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift. Low-resolution mass spectrometry (LRMS) was performed on a JEOL JMS-LCmate liquid chromatography spectrometer system using the APCI+ ionization mode, or a Waters Acquity UPC^2 system using ESI+. High-resolution mass spectrometry (HRMS) was performed on a Xevo G2-XS QTof instrument. Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ). IR spectra were recorded on a Perkin-Elmer FTIR spectrometer. Data for IR are reported as follows: wavenumber (ν, in cm^{-1}), intensity (s=strong, m=moderate, w=weak).

Further Discussion of Nomenclature

Modifications to the simple system embodied by Figure 1 of the manuscript can be made to describe different degrees of substitution and specificity. First, as mentioned briefly in the text, the superbasic core may be decorated by fewer than the maximum possible number of superbasic substituents. When some positions are occupied by simpler, less basic functionalities such as amino or aliphatic groups, the superbasic substituent's subscript designates the number of such superbasic components present, even if the number is unity, and assumes non-superbasic groups at the remaining positions. Thus some partially substituted higher-order superbases are designated as follows: monophosphazenylphosphazenes, P_2; monoguanidinylphosphazenes, PG_1, bisguanidinylphosphazenes, PG_2, and monocyclopropeniminylguanidines, GC_1 (Figure S1a).

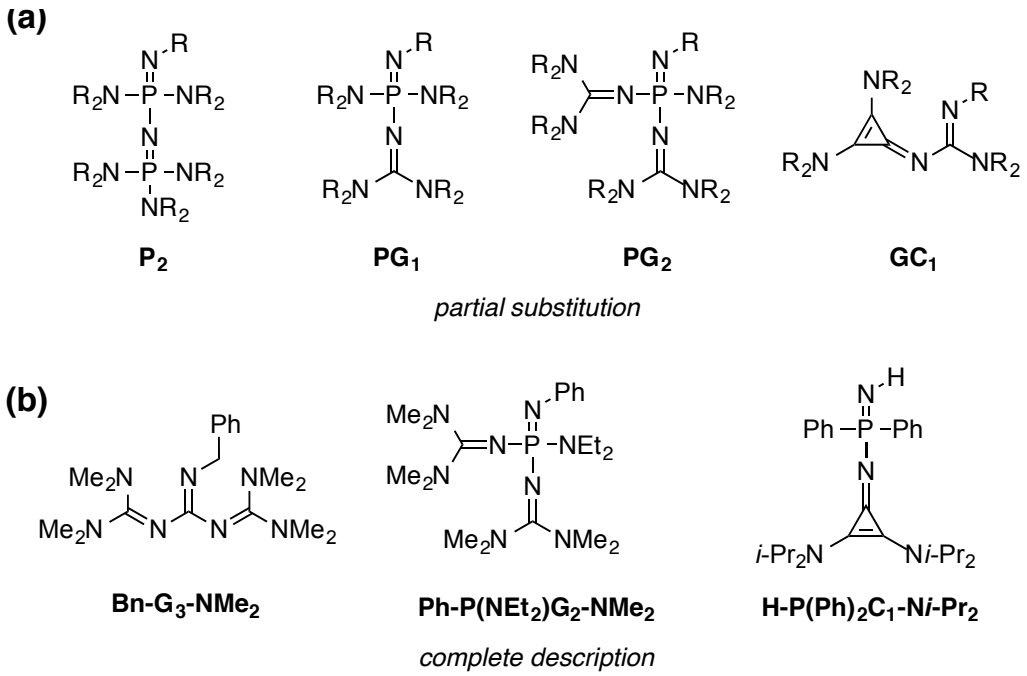
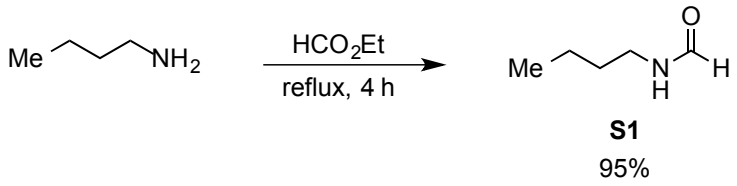


Figure S1. Modifications to simple nomenclature for higher-order superbases, including (a) those with a combination of superbasic and non-superbasic substituents, and (b) a complete description of all groups in the molecule.

Second, the identities of the hydrocarbon derivatives bonded to the superbasic cores and substituents, if desired, are separated by dashes before and after the class of the higher-order superbase, respectively. Any amino substituents bonded to the superbasic core in a partially substituted higher-order superbase are specified in parentheses between the core and substituent letters. Groups bonded to the head imino function should only specify the fragment beyond the nitrogen atom, since a different atom would likely change the base's properties significantly. However, groups at the tail end of the superbasic core or substituents should specify the entire group since deviation from the amino functionality would not necessarily alter the reactivity of the base as dramatically. This latter format (Figure S1b) completely describes the molecule's structure.

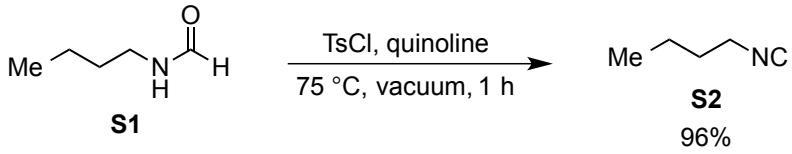
Synthesis of Electrophilic 'Core' Superbase Building Blocks

_N_-Butylformamide (S1):



Based on published procedures,[1,2] ethyl formate (17.7 mL, 220 mmol, 1.10 equiv) was added slowly to butylamine (19.8 mL, 200 mmol, 1.00 equiv) at 0 °C, then heated to 100 °C for 1 hour, and 110 °C for 3 hours. The mixture was concentrated at 35 °C to remove most of the ethanol and unreacted ethyl formate, and distilled (78 °C/3-5 mmHg) to afford a clear, colorless oil (19.32 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) ~3.5:1 mixture of rotamers δ 8.17 (s, 1H, major rotamer), 8.05 (d, J = 12.0 Hz, 1H, minor rotamer), 5.55 (br s, <1H), 3.31 (q, J = 6.7 Hz, 2H, major rotamer), 3.22 (q, J = 6.7 Hz, 2H, minor rotamer), 1.53 (m, 2H), 1.38 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H).

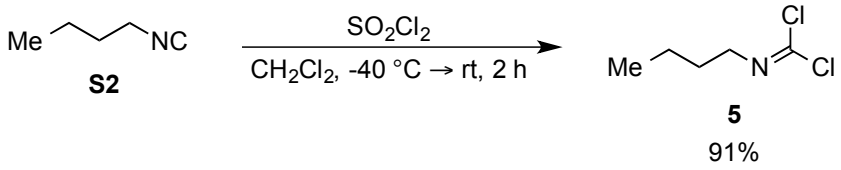
Butyl isocyanide (S2):



Based on published procedures,[1,3] a 500 mL 3-necked flask containing *p*-toluenesulfonyl chloride (54.70 g, 286.9 mmol, 1.50 equiv) and quinoline (91 mL, 770 mmol, 4.0 equiv) was equipped with a magnetic stir bar, an addition funnel, a stopper, and an adapter connecting to a 100 mL Schlenk flask via 1 foot of tubing. The Schlenk flask was cooled to -78 °C and connected to a vacuum line. The reaction was stirred at 75 °C under vacuum (~ 1 mmHg) and *N*-butylformamide (**S1**) (19.3 g, 191 mmol, 1.00 equiv) was added over 40 minutes. The reaction turned yellow, then orange, and finally red during the addition. After another 20 minutes, the condensate was purified by vacuum transfer (~ 1 mmHg) leaving ~ 1 mL of material in the pot to afford a clear, colorless, foul-smelling oil (15.22 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.39 (m, 2H), 1.67 (m, 2H), 1.49 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H).

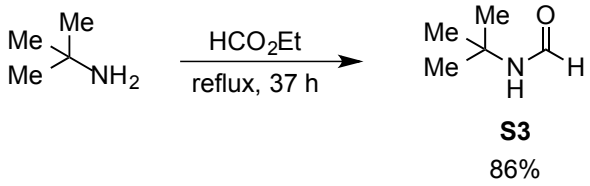
1. Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1988**, *110*, 6818.
2. Moffat, J.; Newton, M. V.; Papenmeier, G. J. *J. Org. Chem.* **1962**, *27*, 4058.
3. Schuster, S. R. E.; Scott, J. E.; Casanova, J.; Dupont, J. A.; Emmons, W. D. *Org. Synth.* **1966**, *46*, 75.

Butyl carbonimidic dichloride (5):



Based on the method of Ganem,[4] a solution of sulfuryl chloride (14.75 mL, 182.0 mmol, 1.00 equiv) in CH_2Cl_2 (35 mL) was added over 1 hour to a solution of butyl isocyanide (**S2**) (19.0 mL, 182 mmol, 1.00 equiv) in CH_2Cl_2 (150 mL) at -40 °C. After another 30 minutes at this temperature, the mixture was warmed to room temperature for 30 minutes and concentrated at 0 °C/40 mmHg to a volume of ~ 25 mL. This residual liquid was distilled (up to 69 °C/40 mmHg, rejecting the first ~ 1 mL) to afford a clear, colorless oil (25.41 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48 (t, J = 6.9 Hz, 2H), 1.63 (m, 2H), 1.38 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.5, 54.8, 31.4, 20.5, 13.8.

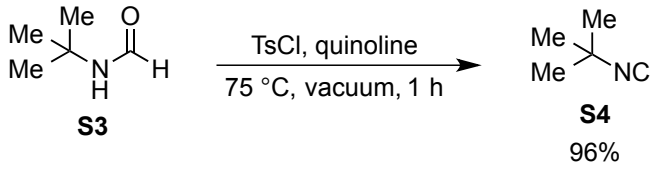
***N-tert*-Butylformamide (S3):**



Similarly to the preparation of **S1**, ethyl formate (51.5 mL, 640 mmol, 1.20 equiv) and *tert*-butylamine (56.0 mL, 533 mmol, 1.00 equiv) were heated in a sealed pressure flask at 100 °C for 37 hours. The mixture was concentrated at 30 °C/20 mmHg to remove most of the ethanol and unreacted ethyl formate, and distilled (70-75 °C/3-5 mmHg) to afford a clear, colorless oil (46.15 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) ~ 1:1 mixture of rotamers δ 8.28 (d, J = 12.4 Hz, 1H), 8.04 (s, 1H), 5.89 (s, 1H), 5.30 (s, 1H), 1.39 (s, 9H), 1.34 (s, 9H).

4. Gober, C. M.; Le, H. V.; Ganem, B. *Tetrahedron Lett*. **2012**, *53*, 4536.

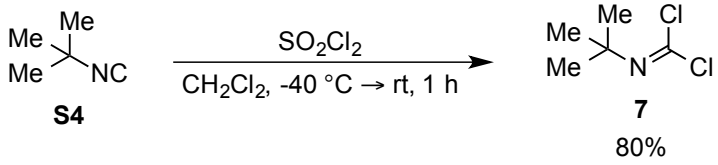
***tert*-Butyl isocyanide (S4):**



S3 **S4** 96%

The same procedure used to prepare **S2** was employed using a slightly smaller scale (*N*-*tert*-butylformamide: 16.7 g, 165 mmol), and the condensate did not require further purification. This operation furnished a clear colorless oil (13.23 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) 1.45 (m, 9H).

***tert*-Butyl carbonimidic dichloride (7):**

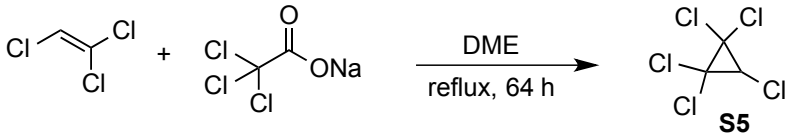


S4 **7** 80%

Based on the method of Ganem,[4] a solution of sulfuryl chloride (12.9 mL, 159 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) was added over 30 minutes to a solution of *tert*-butyl isocyanide (**S4**) (13.2 g, 159 mmol, 1.00 equiv) in CH_2Cl_2 (170 mL) at -40 °C. After another 5 minutes at this temperature, the mixture was warmed to room temperature for 30 minutes and concentrated to a volume of ~ 25 mL. This residual liquid was distilled (62-65 °C/3-5 mmHg) to afford a clear, colorless oil (19.52 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) 1.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 116.4, 60.1, 28.7.

Trichloro-*tert*-butyliminophosphorane (13) was prepared over 2 steps from *tert*-butylamine without modifying the method of Schwesinger.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, J = 2.5 Hz, 9H). ^{31}P NMR (121 MHz, $CDCl_3$) δ -78.97.

Pentachlorocyclopropane (S5):



S5 32%

Based on the method of West,[6] sodium trichloroacetate (775.0 g, 4.055 mol, 1.00 equiv) was crushed to remove any lumps and added to a 5 L flask containing trichloroethylene (1.25 L, 13.9

5. Schwesinger, R.; Willaredt, J.; Schlemper, H.; Keller, M.; Schmitt, D.; Fritz, H. *Chem. Ber.* **1994**, *127*, 2435.

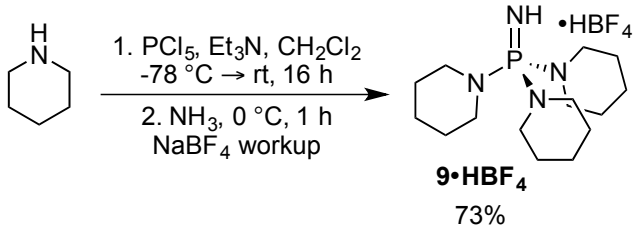
6. Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2478.

mol, 3.44 equiv) and a magnetic stir bar. Two consecutive reflux condensers were attached and left open to the air, the mixture was refluxed behind a blast shield, and 1,2-dimethoxyethane (375 mL) was added. After 64 hours, the mixture was cooled in a freezer for 2 hours, the upper black oil was decanted and the residual silt was suspended in water (3 L) and extracted with CH_2Cl_2 (3 x 500 mL). The combined extracts were added to the decantate. This mixture was dried over $MgSO_4$, concentrated, and distilled through an uncooled reflux condenser (75-83 °C/30 mmHg) to afford a clear, colorless oil (275.7 g, 32%) that was 97% pure as judged by ^{1}H NMR (2% trichloroethylene, 1% DME). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 1H).

Tetrachlorocyclopropene (C_3Cl_4) was prepared from pentachlorocyclopropane (**S5**) and KOH in 50-60% yield without modifying the method of West.[7] ^{13}C NMR (101 MHz, $CDCl_3$) δ 122.7, 62.5.

Synthesis of Nucleophilic 'Substituent' Superbase Building Blocks

Tris(piperidinyl)iminophosphorane P_1 (9)•HBF_4:

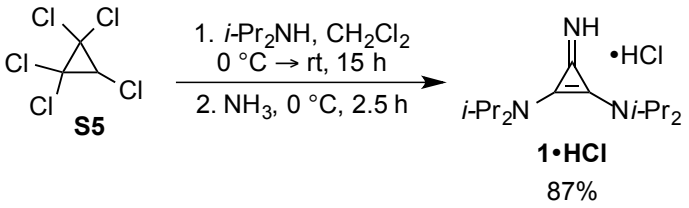


Based on the method of Schwesinger,[8] piperidine (54.7 mL, 554 mmol, 3.00 equiv) was added over 1 hour to a suspension of phosphorus pentachloride (38.5 g, 185 mmol, 1.00 equiv) in CH_2Cl_2 (380 mL) at -78 °C, causing the reaction to turn yellow. Triethylamine (77.2 mL, 554 mmol, 3.00 equiv) was subsequently added over 1 hour at the same temperature, and the solution was stirred for 16 hours further while warming slowly to room temperature. Upon re-cooling to 0 °C, gaseous ammonia was gently bubbled through the rust-colored suspension for 30 minutes, which turned cream-colored during this interval. After stirring for 30 minutes further, the suspension was filtered through celite (50 mL), washed with CH_2Cl_2 (400 mL), and the filtrate was concentrated to afford an orange solid. This solid was dissolved in water (60 mL), stirred, and treated with a solution of $NaBF_4$ (24.4 g, 222 mmol, 1.20 equiv) in water (50 mL), immediately causing a large amount of material to precipitate. The slurry was filtered and the solid was air-dried for 3 hours. To remove residual triethylamine, the solids were dissolved in CH_2Cl_2 (300 mL), washed with 5% Na_2CO_3 (100 mL), the aqueous layer was saturated with $NaBF_4$ and extracted with CH_2Cl_2 (25 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated. The solid residue was recrystallized from EtOAc (600 mL) to afford a flaky orange solid (52.24 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.06 (d, J = 6.7 Hz, 2H), 3.10 (m, 12H), 1.60 (m, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 45.9 (d, J_{PC} = 1.8 Hz), 25.7 (d, J_{PC} = 4.7 Hz), 24.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.4. LRMS (APCI+) for $C_{15}H_{31}N_4P$ $[MH]^+$ m/z calcd 299.24, found 299.22. IR (ATR) ν 3385 (w), 3300 (w), 2928 (w), 2855 (w), 1572 (w), 1455 (w), 1372 (m), 1344 (m), 1283 (w), 1206 (m), 1170 (s), 1112 (m), 1077 (s), 1056 (s), 1028

7. Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2481.

(s), 1012 (s), 955 (s), 928 (m), 895 (w), 855 (m), 834 (w), 728 (m), 716 (w), 637 (w), 556 (w), 521 (w), 471 (m), 439 (m).

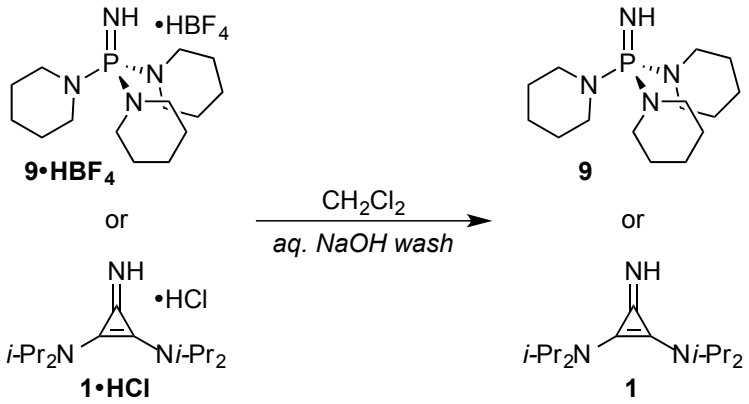
2,3-Bis(diisopropylamino)cyclopropenimine C_1 (1)•HCl:



Diisopropylamine (120 mL, 860 mmol, 6.5 equiv) was added over 2 hours via an addition funnel to a solution of pentachlorocyclopropane (**S5**) (33.34 g, 85%, 132 mmol, 1.00 equiv) in CH_2Cl_2 (1.5 L) at 0 °C, and the solution was stirred for 15 hours further while warming slowly to room temperature. Upon re-cooling to 0 °C, ammonia was gently bubbled through the suspension for 30 minutes, followed by more vigorous bubbling for 30 minutes. After stirring for 1 hour further, the suspension was filtered through celite (150 mL), washed with CH_2Cl_2 (300 mL), and the filtrate was concentrated to afford a tan-orange solid. This material was dissolved in water (2 L), treated with Na_2CO_3 (79 g, 750 mmol, 5.6 equiv), washed with EtOAc (6 x 200 mL) until the aqueous layer was pale yellow, saturated with NaCl, and extracted with CH_2Cl_2 (3 x 350 mL). The combined CH_2Cl_2 extracts were then dried over Na_2SO_4 and concentrated to afford a light yellow solid. This crude solid was recrystallized from ~ 3:1 EtOAc/CH_2Cl_2 (550 mL) and slowly evaporated over 5 days to a volume of 500 mL, followed by standing at -20 °C for 3 weeks to yield large colorless prisms (33.1 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 2H), 3.79 (hept, J = 6.7 Hz, 24H), 1.34 (d, J = 6.9 Hz, 24H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 116.1, 113.1, 50.6, 22.5. LRMS (APCI+) for $C_{15}H_{29}N_3$ $[MH]^+$ m/z calcd 252.24, found 252.25. IR (ATR) ν 2974 (w), 1635 (m), 1506 (s), 1453 (m), 1358 (s), 1214 (m), 1195 (m), 1152 (m), 1136 (m), 1048 (w), 992 (w), 943 (w), 892 (w), 718 (m), 612 (w), 561 (w), 503 (m).

8. Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H. W.; Bordwell, F. G.; Satish, A. V.; Ji, G.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Walz, L. *Liebigs Ann*. **1996**, 1055.

Liberation of nucleophilic 'substituent' building blocks as free bases on scale



Salts of compounds **9** or **1** (up to 10 g) were dissolved in CH_2Cl_2 (0.03-0.1 M) and washed with 1-3 M NaOH (3 x 50-80 equiv), dried over K_2CO_3, and concentrated. Free base **1** was obtained as an air-stable white solid in 90-98% yields and could be weighed on the bench. In contrast, **9** was obtained as a pale orange oil that decomposed more quickly in air, so it was concentrated and subsequently handled under inert atmosphere; amounts were calculated based the quantity of the HBF_4 salt initially employed.

Evaluation of the extent of deprotonation by the above procedure

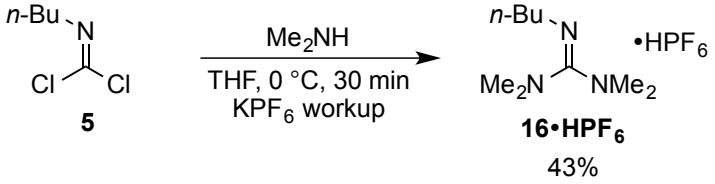
Samples of **9** and **1** salts in CD_3CN gave NMR spectra of the fully protonated forms of these superbases.

To generate the fully deprotonated free bases, CD_3CN solutions (0.1 M) of these salts were stirred with KO*t*-Bu (5-6 equiv) under argon for 30 minutes and quickly filtered into NMR tubes. The resulting NMR spectra were assumed to deprotonate the superbases quantitatively (the internally consistent application of this method to generate free bases in the pK_{BH+} determination section validated this method).

Finally, samples obtained from the aqueous NaOH washing procedure were dissolved in CD_3CN and compared to the fully protonated and fully deprotonated forms. NMR spectra from these experiments are included following the $CDCl_3$ spectra of the conjugate acids. This comparison indicated that the aqueous NaOH washes gave **9** as 98% deprotonated and **1** as 95% deprotonated.

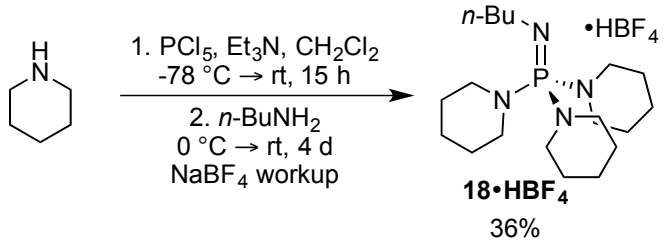
Synthesis of First-Order Superbases

N^1-butyl-N^2, N^2, N^3, N^3-tetramethylguanidine G_1 (16)•HPF_6:[9]



Dimethylamine (excess) was gently bubbled through a solution of butyl carbonimidic dichloride (**5**) (0.77 g, 5.0 mmol, 1.0 equiv) in THF (40 mL) for 10 minutes. A precipitate formed, and after 20 minutes further, the mixture was concentrated and dissolved in CH_2Cl_2 (30 mL). This solution was washed with KPF_6 (1.85 g, 10 mmol, 2.0 equiv) in 5% Na_2CO_3 (30 mL), the aqueous layer was extracted with CH_2Cl_2 (10 mL), and the combined organic extracts were washed with 0.25 M KPF_6 (20 mL), dried over Na_2SO_4, and concentrated. The residue was dissolved in toluene (4 mL) and a minimum of CH_2Cl_2 (~ 4 mL), and hexanes was diffused into this solution at -20 °C for 2 days, forming a biphasic mixture. The resulting system was stirred at -78 °C for 2 hours and filtered to afford a white solid (687 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (br s, 1H), 3.18 (dt, J = 7.3, 5.8 Hz, 2H), 2.99 (s, 12H), 1.62 (m, 2H), 1.36 (hex, J = 7.5 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 45.4, 39.8, 31.9, 19.9, 13.7. LRMS (APCI+) for $C_9H_{21}N_3$ $[MH]^+$ m/z calcd 172.18, found 172.19. IR (ATR) ν 3395 (w), 3148 (w), 2973 (w), 2937 (w), 1618 (m), 1586 (m), 1509 (m), 1455 (m), 1404 (w), 1371 (w), 1346 (w), 1215 (w), 1193 (w), 1150 (w), 1135 (w), 1042 (m), 840 (s), 826 (s), 556 (s), 499 (w).

Tris(piperidinyl)(butylimino)phosphorane P_1 (18)•HBF_4:

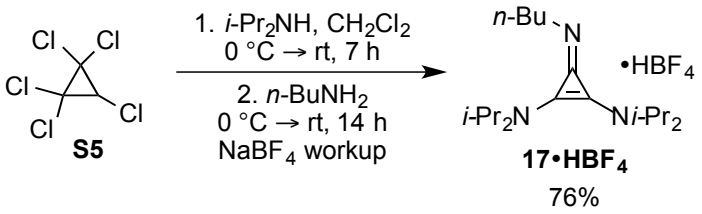


Based on the method of Schwesinger,[8] piperidine (2.95 mL, 29.9 mmol, 3.00 equiv) was added over 1 hour to a suspension of phosphorus pentachloride (2.07 g, 9.94 mmol, 1.00 equiv) in CH_2Cl_2 (25 mL) at -78 °C, causing the reaction to turn yellow. Triethylamine (4.20 mL, 30.1 mmol, 3.03 equiv) was subsequently added over 1 hour at the same temperature, and the solution was stirred for 14 hours further while warming slowly to room temperature. Upon re-cooling to 0 °C, CH_2Cl_2 (15 mL) and butylamine (2.95 mL, 29.9 mmol, 3.00 equiv) were added. After warming slowly to room temperature, stirring for 4 days further, the solution was diluted with CH_2Cl_2 (35 mL), washed with 1 M HCl (3 x 15 mL), each wash was extracted with CH_2Cl_2 (5 mL), and the combined organic layers were concentrated. The residue was dissolved in 5%

9. Li, S.; Lin, Y.; Xie, H.; Zhang, S.; Xu, J. *Org*. *Lett*. **2006**, *8*, 391.

Na_2CO_3 (25 mL), washed with diethyl ether (2 x 10 mL), treated with $NaBF_4$ (2.20 g, 20.0 mmol, 2.01 equiv), extracted into CH_2Cl_2 (3 x 15 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated to leave a yellow semisolid. Recrystallization from ~ 2:1 EtOAc/hexanes (20 mL), after evaporating to a volume of ~ 5 mL provided the phosphazene•HBF_4 as a white solid (1.60 g, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38(m, 1H), 3.11 (m, 12H), 2.90 (m, 2H), 1.73 – 1.48 (overlapping signals, 20H), 1.35 (hex, J = 7.4 Hz 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 46.2, 41.4, 33.3 (d, J_{PC} = 6.7 Hz), 25.6 (d, J_{PC} = 4.8 Hz), 23.8, 19.8, 13.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.4. LRMS (APCI+) for $C_{19}H_{39}N_4P$ $[MH]^+$ m/z calcd 355.30, found 355.29. IR (ATR) ν 3319 (w), 2960 (w), 2935 (w), 2862 (w), 1618 (w), 1587 (w), 1508 (m), 1454 (m), 1370 (m), 1346 (m), 1212 (w), 1167 (m), 1125 (w), 1103 (m), 1062 (s), 1024 (s), 958 (s), 838 (s), 717 (m), 558 (m), 520 (w), 501 (w), 465 (w), 442 (w).

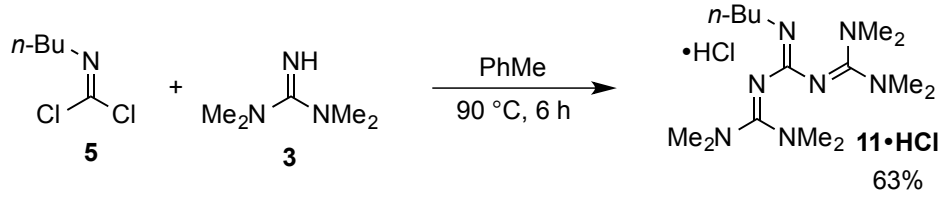
2,3-Bis(diisopropylamino)-*N*-butylcyclopropenimine C_1 (17)•HBF_4:



Diisopropylamine (8.7 mL, 62 mmol, 6.0 equiv) was added over 1 hour to a solution of pentachlorocyclopropane (**S5**) (1.33 mL, 10.4 mmol, 1.00 equiv) in CH_2Cl_2 (75 mL) at 0 °C, and the solution was stirred for 6 hours further while warming slowly to room temperature. Upon re-cooling to 0 °C, butylamine (3.1 mL, 31 mmol, 3.0 equiv) was added and the mixture was stirred for 14 hours further. This solution was then washed with sat. NH_4Cl (2 x 40 mL) and a combination of 0.5 M Na_2CO_3 and 1 M $NaBF_4$ (2 x 20 mL), dried over Na_2SO_4, and concentrated to afford an orange solid that was recrystallized twice from 2:1 EtOAc/hexanes (50 mL) to yield a coarse white solid (3.11 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (br s, 1H), 3.81 (hept, J = 6.9 Hz, 4H), 3.44 (dt, J = 7.4, 6.2 Hz, 2H), 1.68 (m, 2H), 1.45 – 1.24 (overlapping signals, 26H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 116.3, 113.8, 50.7, 46.6, 32.9, 22.0, 19.7, 13.7. LRMS (APCI+) for $C_{19}H_{37}N_7$ $[MH]^+$ m/z calcd 308.31, found 308.28. IR (ATR) ν 3329 (w), 2972 (w), 2937 (w), 2873 (w), 1521 (s), 1454 (w), 1371 (w), 1344 (m), 1213 (w), 1193 (w), 1156 (w), 1140 (w), 1066 (s), 1010 (s), 636 (w), 559 (w), 520 (w), 501 (w).

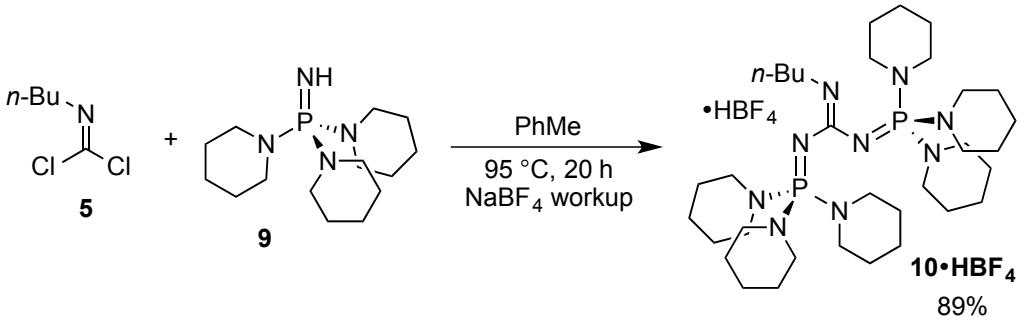
Synthesis of Second-Order Superbases

Bis(N^2, N^2, N^3, N^3-tetramethylguanidinyl)-*N*-butylimine G_3 (11)•HCl:



A mixture of tetramethylguanidine (**3**) (8.20 mL, 65.4 mmol, 3.26 equiv) and butyl carbonimidic dichloride (**5**) (3.09 g, 20.1 mmol, 1.00 equiv) in toluene (45 mL) was heated at 90 °C for 6 hours. The resulting slurry was filtered and washed with toluene (50 mL), and the filtrate was concentrated. The filtrate and the solid residues were separately dissolved in CH_2Cl_2 (75 mL), washed with sat. NH_4Cl (3 x 35 mL), dried over Na_2SO_4, and concentrated. Each residue was then recrystallized from EtOAc (solid, 200 mL; filtrate, 50 mL) to provide two crops of spectroscopically identical white solids. The material was combined and again recrystallized from EtOAc (225 mL) to provide the triguanide•HCl as a white solid (4.37 g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 3.32 (app q, 2H), 2.92 (app d, 24H), 1.68 (m, 2H), 1.39 (hex, J = 7.5 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 162.6, 161.5, 42.6, 40.1, 39.9, 31.8, 20.3, 13.8. LRMS (APCI+) for $C_{15}H_{33}N_7$ $[MH]^+$ m/z calcd 312.29, found 312.26. IR (ATR) ν 3329 (w), 2969 (w), 2936 (w), 2873 (w), 1518 (s), 1455 (m), 1374 (m), 1344 (m), 1213 (w), 1193 (w), 1157 (m), 1140 (m), 1061 (s), 1026 (s), 1011 (s), 960 (w), 718 (w), 559 (w), 520 (w), 500 (w).

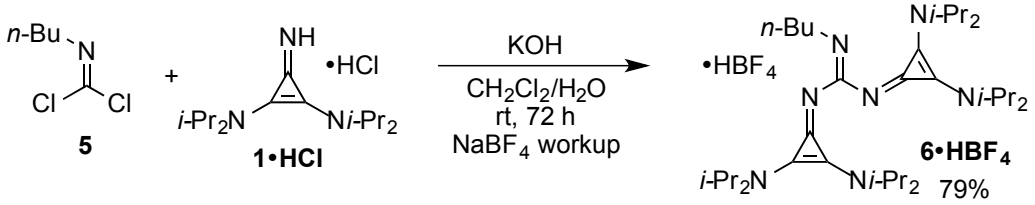
Bis(tris(piperidinyl)iminophosphoranyl)-*N*-butylimine GP_2 (10)•HBF_4:



A mixture of phosphazene **9** (from 5.79 g of the HBF_4 salt, 15.0 mmol, 5.00 equiv) and butyl carbonimidic dichloride (**5**) (462 mg, 3.00 mmol, 1.00 equiv) in toluene (50 mL) was heated at 95 °C for 20 hours. The resulting slurry was diluted with toluene (50 mL), washed with 25% sat. NH_4Cl (3 x 50 mL), sat. $NaHCO_3$ (2 x 25 mL), and 1 M $NaBF_4$ (2 x 25 mL), dried over Na_2SO_4, and concentrated. The resulting solid was recrystallized by diffusion of hexanes into a saturated solution of hot toluene (15 mL) for 2 days at -20 °C to provide a white solid (2.04 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (m, 1H), 3.26 (dt, J = 7.3, 5.8 Hz, 2H), 3.07 (s, 24H), 1.72 – 1.43 (overlapping signals, 38H), 1.33 (hex, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 46.5 (d, J_{PC} = 17.6 Hz), 43.2, 32.0, 26.3, 24.4 (d, J_{PC} = 29.3 Hz),

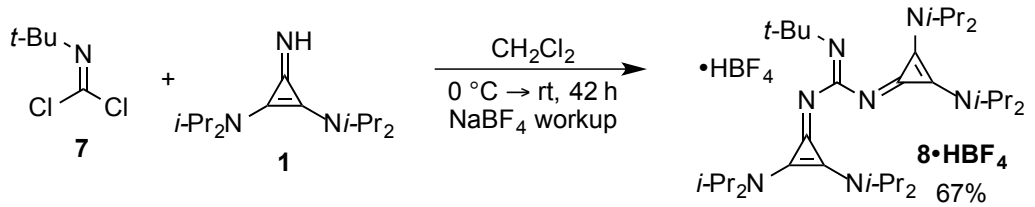
20.3, 14.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.6, 19.8. HRMS (APCI+) for $C_{35}H_{69}N_9P_2$ $[MH]^+$ m/z calcd 678.5229, found 678.5246. Elemental analysis for $C_{35}H_{70}N_9P_2BF_4$ calcd 54.90% C, 9.21% H, 16.46% N, found 54.73% C, 9.49% H, 16.28% N. IR (ATR) ν 3182 (w), 2932 (w), 2872 (w), 1523 (m), 1474 (m), 1452 (m), 1400 (m), 1375 (s), 1345 (m), 1311 (w), 1230 (w), 1209 (w), 1166 (m), 1053 (s), 1033 (s), 951 (m), 900 (w), 859 (w), 835 (w), 807 (w), 756 (w), 725 (w), 676 (w), 615 (w), 567 (w), 520 (w).

Bis(2,3-bis(diisopropylamino)cyclopropeniminyl)-*N*-butylimine GC_2 (6)•HBF_4:



A 3 M solution of potassium hydroxide (13.75 mL, 41.25 mmol, 4.04 equiv) was added to a solution of cyclopropenimine **1**•HCl (5.88 g, 20.4 mmol, 2.00 equiv) and butyl carbonimidic dichloride (**5**) (1.65 g, 10.7 mmol, 1.00 equiv) in CH_2Cl_2 (100 mL) at 0 °C. After stirring for 72 hours, the CH_2Cl_2 was evaporated, the residue was dissolved in EtOAc (250 mL), extracted with 1 M HCl (3 x 75 mL), and extracted from the combined aqueous layers with CH_2Cl_2 (3 x 75 mL). The combined CH_2Cl_2 layers were washed with 5% Na_2CO_3 (75 mL) and concentrated. This residue was dissolved in EtOAc (150 mL), washed with sat. NH_4Cl (50 mL), 50% sat. NH_4Cl (2 x 50 mL), and a combination of 5% Na_2CO_3 and 1 M $NaBF_4$ (2 x 25 mL), dried over Na_2SO_4, and concentrated. The resulting pale yellow solid was recrystallized from ~ 10:1 EtOAc/hexanes (125 mL) for 6 days at -20 °C to provide a white solid (5.67 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.52 (t, J = 5.6 Hz, 1H), 3.89 (hept, J = 6.7 Hz, 8H), 3.31 (dt, J = 7.4, 5.8 Hz, 2H), 1.59 (m, 2H), 1.39 – 1.18 (overlapping signals, 50H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 121.9, 120.4, 50.3, 42.9, 32.1, 22.1, 20.3, 14.0. HRMS (ESI+) for $C_{35}H_{65}N_7$ $[MH]^+$ m/z calcd 584.5380, found 584.5374. IR (ATR) ν 3389 (w), 3188 (w), 2974 (w), 2934 (w), 2874 (w), 1508 (m), 1484 (m), 1452 (m), 1422 (m), 1372 (m), 1340 (s), 1215 (w), 1161 (m), 1092 (m), 1043 (s), 1032 (s), 956 (w), 932 (w), 900 (w), 757 (w), 723 (w), 680 (w), 614 (w), 571 (w), 518 (w), 504 (w).

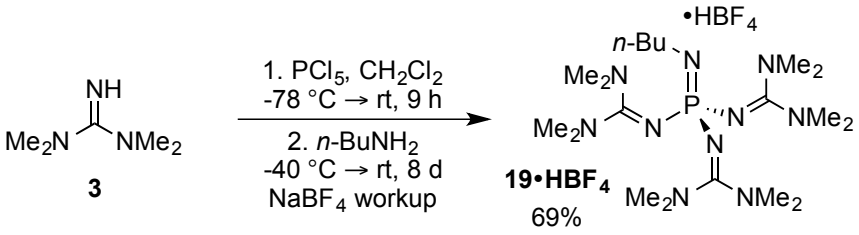
Bis(2,3-bis(diisopropylamino)cyclopropeniminyl)-*N*-*tert*-butylimine GC_2 (8)•HBF_4:



A solution of *tert*-butyl carbonimidic dichloride (**7**) (1.17 g, 7.60 mmol, 1.00 equiv) in CH_2Cl_2 (8 mL) was added to a solution of cyclopropenimine **1** (7.68 g, 30.6 mmol, 4.02 equiv) in CH_2Cl_2 (200 mL) at 0 °C. After stirring for 42 hours, the CH_2Cl_2 was evaporated, the residue was suspended in EtOAc (200 mL), washed with 50% sat. NH_4Cl (2 x 75 mL) and a combination of

5% Na_2CO_3 and 1 M $NaBF_4$ (2 x 25 mL), dried over Na_2SO_4, and concentrated. This solid was recrystallized from ~ 2:1 EtOAc/hexanes (50 mL) for 2 days at -20 °C to provide a white solid (3.44 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.09 (s, 1H), 3.87 (hept, J = 6.8 Hz, 8H), 1.43 (s, 9H), 1.29 (d, J = 6.8 Hz, 48H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 121.5, 120.4, 51.9, 50.3, 29.3, 22.1. HRMS (ESI+) for $C_{35}H_{65}N_7$ $[MH]^+$ m/z calcd 584.5380, found 584.5374.

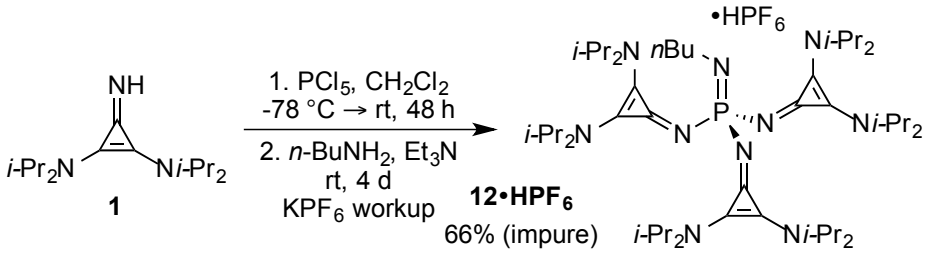
Tris(N^2, N^2, N^3, N^3-tetramethylguanidinyl)(butylimino)phosphorane PG_3 (19)•HBF_4:



Based on the method of Kolomeitsev and coworkers,[10] tetramethylguanidine (**3**) (3.78 mL, 29.9 mmol, 6.00 equiv) was added over 30 minutes to a suspension of phosphorus pentachloride (1.07 g, 5.14 mmol, 1.02 equiv) in CH_2Cl_2 (50 mL) at -78 °C,and warmed slowly to room temperature over 9 hours. Upon re-cooling to -40 °C, butylamine (2.30 mL, 23.3 mmol, 4.53 equiv) was added. After warming slowly to room temperature, stirring for 8 days further, the solution was washed with sat. NH_4Cl (2 x 25 mL), 2 M Na_2CO_3 (20 mL), and a combination of 0.5 M Na_2CO_3 and 1 M $NaBF_4$ (2 x 10 mL), dried over Na_2SO_4, and concentrated and the combined organic layers were concentrated. The resulting white solid was filtered through silica gel (30 mL) with 5% methanol/CH_2Cl_2 (1.5 L), concentrated, and recrystallized from ~ 2:1 EtOAc/hexanes (15 mL) while diffusing in further hexanes at -20 °C to provide the phosphazene•HBF_4 as a white solid (1.89 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (s, 36H), 2.74 (quint, J = 7.1 Hz, 2H), 2.38 (app q, 1H), 1.46 (m, 2H), 1.31 (hex, J = 7.4, 2H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 41.1, 40.3, 34.0, 33.9, 20.2, 13.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -9.42. LRMS (APCI+) for $C_{19}H_{45}N_{10}P$ $[MH]^+$ m/z calcd 445.36, found 455.38. IR (ATR) ν 3331 (w), 2961 (w), 2936 (w), 2873 (w), 1516 (s), 1468 (m), 1418 (m), 1403 (m), 1378 (m), 1342 (m), 1234 (w), 1213 (w), 1195 (w), 1146 (m), 1101 (m), 1053 (s), 1032 (s), 918 (m), 900 (s), 755 (w), 667 (m), 638 (w), 591 (w), 547 (w), 520 (w), 462 (w), 435 (w).

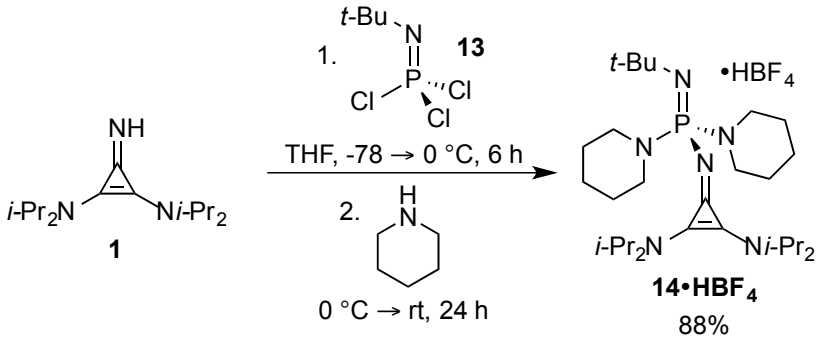
10. Kolomeitsev, A. A.; Koppel, I. A.; Rodima, T.; Barten, J.; Lork, E.; Röschenthaler, G.-V.; Kaljurand, I.; Kütt, A.; Koppel, I.; Mäemets, V.; Leito, I. *J. Am. Chem. Soc.* **2005**, *127*, 17656.

Tris(2,3-bis(diisopropylamino)cyclopropeniminyl)(butylimino)phosphorane PC_3 (12)•HPF_6:



A solution of cyclopropenimine **1** (5.29 g, 21.0 mmol, 6.05 equiv) in CH_2Cl_2 (20 mL) was added over 2 hours to a suspension of phosphorus pentachloride (724 mg, 3.48 mmol, 1.00 equiv) in CH_2Cl_2 (15 mL) at -78 °C, and warmed slowly to room temperature. After 48 hours, butylamine (0.70 mL, 7.1 mmol, 2.0 equiv) and triethylamine (1.5 mL, 11 mmol, 3.1 equiv) were added and the mixture was stirred for 4 days. The solution was then concentrated, suspended in EtOAc (100 mL), and filtered, and the filtrate was washed with sat. NH_4Cl (2 x 25 mL) and a combination of 0.5 M Na_2CO_3 and 0.5 M KPF_6 (2 x 20 mL), dried over Na_2SO_4, and concentrated. The resulting yellow solid (3.09 g) was judged to be 74% pure vs. an internal Bn_2O ^1H NMR standard representing a yield of 66%. All attempts to purify this material by chromatography on silica or alumina gel, or by recrystallization from a variety of solvents at an array of concentrations and temperatures either gave a negligible improvement in purity or decomposed the material further, so this impure mixture was partially characterized (NMR spectra are included), and its pK_{BH+} could not be determined. The following data was tentatively assigned to the title compound: ^1H NMR (500 MHz, $CDCl_3$) δ 3.92 (quint, J = 6.8 Hz, 12H), 2.87 (m, 2H), 2.80 (m, 1H), 0.84 (t, J = 7.3 Hz, 3H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.57. LRMS (APCI+) for $C_{49}H_{93}N_{10}P$ $[MH]^+$ m/z calcd 853.74, found 853.86.

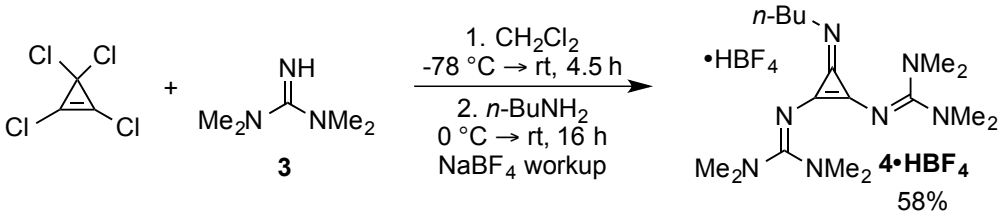
2,3-Bis(diisopropylamino)cyclopropeniminyl-bis(piperidinyl)-(*tert*-butylimino)phosphorane PC_1 (14)•HBF_4:



A solution of trichlorophosphorane **13** (1.05 g, 5.04 mmol, 1.00 equiv) in THF (5 mL) was added dropwise to a solution of cyclopropenimine **1** (2.82 g, 11.2 mmol, 2.23 equiv) in THF (70 mL) at -78 °C. After 4 hours, the reaction was warmed to 0°C, and after 2 hours at this temperature, piperidine (2.5 mL, 25 mmol, 5.0 equiv) was added. After 24 hours further while warming to room temperature, the reaction was concentrated, and the residue was suspended in EtOAc (150

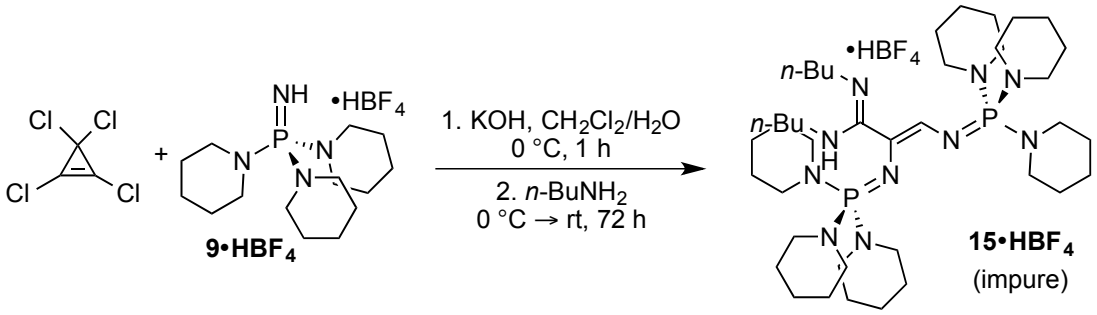
mL), washed with sat. NH_4Cl (2 x 75 mL), 50% sat. NH_4Cl (75 mL), and a combination of 0.5 M Na_2CO_3 and 1 M $NaBF_4$ (2 x 20 mL), dried over Na_2SO_4, and concentrated. The resulting yellow solid (3.21 g) was recrystallized from ~ 2:1 EtOAc/hexanes (100 mL) while diffusing in further hexanes at -20 °C to provide the phosphazene•HBF_4 as a white solid (2.71 g, 88%).[1]H NMR (500 MHz, $CDCl_3$) δ 3.92 (hept, J = 6.9 Hz, 4H), 3.28 (d, J = 12.1 Hz, 1H), 3.19 (m, 4H), 3.08 (m, 4H), 1.63 – 1.52 (m, 12H), 1.33 (d, J = 7.0 Hz, 24H), 1.29 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 119.4 (d, J_{PC} = 22.1 Hz), 118.5, 52.1, 49.7, 46.2, 31.4 (d, J_{PC} = 3.9 Hz), 26.1 (d, J_{PC} = 5.3 Hz), 24.4, 22.0. ^{31}P NMR (121 MHz, $CDCl_3$) δ 16.18. HRMS (ESI+) for $C_{29}H_{57}N_6P$ $[MH]^+$ m/z calcd 521.4461, found 521.4469.

Bis(N^2, N^2, N^3, N^3-tetramethylguanidinyl)-*N*-butylcyclopropenimine CG_2 (4)•HBF_4:



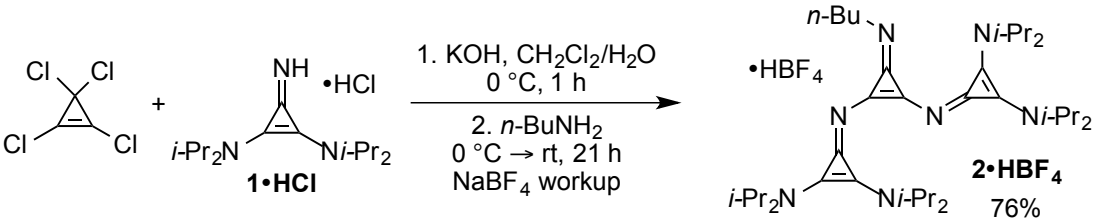
A solution of tetramethylguanidine (**3**) in CH_2Cl_2 (5.50 mL TMG diluted to a volume of 19.6 mL, used 18.2 mL, 40.7 mmol TMG, 3.99 equiv) was added at -78 °C over 1 hour to a solution of tetrachlorocyclopropene (1.25 mL, 10.2 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL). After stirring for 3 hours further at this temperature, the reaction was warmed to room temperature for 30 minutes, cooled to 0°C, and butylamine (2.5 mL, 25 mmol, 2.5 equiv) was added. After 16 hours, the reaction was concentrated, redissolved in 1:1 EtOAc/CH_2Cl_2,, and extracted into sat. NH_4Cl (3 x 40 mL). The combined aqueous extracts were washed with CH_2Cl_2 (3 x 40 mL), then these combined organic layers were washed with sat. NH_4Cl (2 x 30 mL) and a combination of 0.5 M Na_2CO_3 and 1 M $NaBF_4$ (2 x 20 mL), dried over Na_2SO_4, and concentrated. The resulting brown syrup was purified by flash chromatography (5% → 8% methanol/CH_2Cl_2) on silica gel (250 mL) to provide a yellow semisolid. This material was recrystallized from ~ 4:1 EtOAc/hexanes (30 mL) while diffusing in further hexanes at -20 °C to provide the HBF_4 salt of the title compound as a yellow solid (2.51 g, 58%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.58 (t, J = 5.3 Hz, 1H), 3.36 (app q, 2H), 2.96 (s, 24H), 1.67 (m, 2H), 1.38 (hex, J = 7.5 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 128.5, 124.4, 123.4, 46.3, 39.8, 32.2, 19.3, 13.5. HRMS (ESI+) for $C_{17}H_{33}N_7$ $[MH]^+$ m/z calcd 336.2876, found 336.2881. Elemental analysis for $C_{17}H_{34}N_7BF_4$ calcd 48.24% C, 8.10% H, 23.16% N, found 48.21% C, 8.37% H, 22.98% N. IR (ATR) ν 3349 (w), 3182 (w), 2933 (w), 2874 (w), 1522 (m), 1474 (m), 1444 (m), 1427 (m), 1402 (m), 1377 (s), 1346 (m), 1311 (w), 1230 (w), 1167 (w), 1146 (w), 1092 (m), 1046 (s), 1033 (s), 1000 (m), 920 (w), 901 (m), 806 (w), 756 (w), 680 (w), 616 (w), 567 (w), 520 (w), 420 (w), 520 (w), 463 (w), 435 (w).

2,3-Bis(tris(piperidinyl)iminophosphoranyl)-*N*^{1},*N*^{2}-dibutylacrylamidine (15)•HBF$_4$:



A 3 M solution of potassium hydroxide (2.00 mL, 6.00 mmol, 3.98 equiv) was added to a solution of phosphazene **9**•HBF_4 (1.16 g, 3.00 mmol, 1.9 equiv) and tetrachlorocyclopropene (185 µL, 1.51 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) at 0 °C. After stirring for 1 hour, the layers were separated; the organic layer was dried over Na_2SO_4, and quickly filtered into a second dry flask under argon at 0 °C. Butylamine (0.74 mL, 7.5 mmol, 5.0 equiv) was added and the solution was stirred for 72 hours further while warming slowly to room temperature. The reaction was then washed with 5% Na_2CO_3 (3 x 25 mL), dried over Na_2SO_4, and concentrated. The residue was purified by chromatography (CH_2Cl_2 → 5% methanol/CH_2Cl_2) on neutral alumina (125 mL) and recrystallized from EtOAc (5 mL) while slowly diffusing in hexanes over 2 weeks to afford a light peach solid (1.28 g, yield not determined). This procedure gave the highest purity of the major product, albeit still contaminated with an unidentified compound. No evidence was found for the desired bis(phosphazenyl)cyclopropenimine. The NMR spectra of the mixture are included, and the following data are tentatively used to assign the title structure: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.67 (app. q, *J* = 6.9 Hz, 1H), 4.62 (t, *J* = 4.8 Hz, 1H), 4.09 (d, *J* = 7.4 Hz, 1H), 3.29 (q, *J* = 6.8 Hz, 2H), 3.15 – 3.00 (overlapping signals, contains 24H from piperidinyl groups and the NC**H$_2$** for one butyl residue), 1.73 – 1.43 (overlapping signals, contains 36H from piperidinyl groups and the NCH_2C**H$_2$** for both butyl residues), 1.40 (m, 2H), 1.34 (m, 2H with some overlap), 0.95 (t, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 7.4 Hz, 3H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.90, 19.17. LRMS (APCI+) for $C_{43}H_{82}N_8P_2$ $[MH]^+$ m/z calcd 773.62, found 773.63.

Bis(2,3-bis(diisopropylamino)cyclopropeniminyl)-*N*-butylcyclopropenimine C$_3$ (2)•HBF$_4$:



A 3 M solution of potassium hydroxide (20.25 mL, 60.75 mmol, 4.03 equiv) was added to a solution of cyclopropenimine **1**•HCl (8.71 g, 30.3 mmol, 2.01 equiv) and tetrachlorocyclopropene (1.85 mL, 15.1 mmol, 1.00 equiv) in CH_2Cl_2 (300 mL) at 0 °C. After stirring for 1 hour, the layers were separated; the organic layer was dried over Na_2SO_4, and quickly filtered into a second flask at 0 °C. Butylamine (1.4 mL, 14 mmol, 4.8 equiv) was added

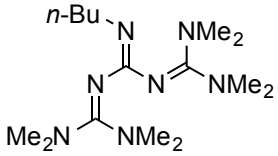
and the solution was stirred for 21 hours further while warming slowly to room temperature. The reaction was then washed with a combination of 0.5 M Na_2CO_3 and 0.5 M $NaBF_4$ (2 x 100 mL), dried over Na_2SO_4, and concentrated. The residue was redissolved in EtOAc (300 mL), washed with sat. NH_4Cl (3 x 50 mL) and a combination of 0.5 M Na_2CO_3 and 1 M $NaBF_4$ (50 mL), dried over Na_2SO_4, and concentrated to provide a tan solid (11.75 g). This material was dissolved in hot EtOAc (125 mL), cooled to room temperature, and hexanes was diffused in for 3 days, followed by standing at -20 °C overnight. The product crystallized as large yellow prisms (8.00 g) that were spectroscopically pure, although the recrystallization was repeated on ~ 80% of the previous scale and deposited white prisms (7.93 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (s, 1H), 3.84 (hept, J = 6.7 Hz, 8H), 3.30 (app q, 2H), 1.66 (m, 2H), 1.42 – 1.18 (overlapping signals, 50H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.0, 124.2, 122.3, 119.7, 50.2, 46.5, 32.7, 21.9, 19.6, 13.6. HRMS (ESI+) for $C_{37}H_{65}N_7$ $[MH]^+$ m/z calcd 608.5380, found 608.5383. Elemental analysis for $C_{37}H_{66}N_7BF_4$ calcd 63.87% C, 9.56% H, 14.09% N, found 63.59% C, 9.76% H, 13.98% N. IR (ATR) ν 3337 (w), 2972 (w), 2935 (w), 2874 (w), 1501 (s), 1470 (m), 1453 (m), 1432 (s), 1405 (m), 1384 (m), 1334 (s), 1241 (w), 1217 (m), 1192 (m), 1161 (m), 1133 (m), 1106 (w), 1063 (s), 1024 (s), 884 (w), 839 (w), 763 (w), 741 (w), 660 (w), 581 (w), 554 (w), 516 (w), 503 (w).

Liberation of Higher-Order Superbases

In a glove box, a solution of KO*t*-Bu (1 M in THF, 1.0 equiv) was added to a solution of superbase conjugate acid salt in THF (~ 0.2 M) at room temperature. After 5-10 minutes, the solution was filtered (0.2 μm PTFE), washed with THF, concentrated, redissolved in PhMe, filtered again, and concentrated.

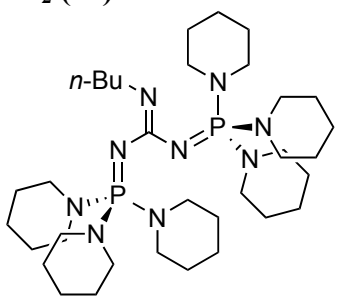
Attempts to perform this procedure on a vacuum line invariably failed, with trace to moderate decomposition occurring, likely due to the modest lower limit of our vacuum pressures (~ 1 mmHg). Due to the impracticality of this procedure compared to deprotonation *in situ* for synthetic purposes, we typically only liberated smaller quantities of free bases for characterization.

G_3 (11)



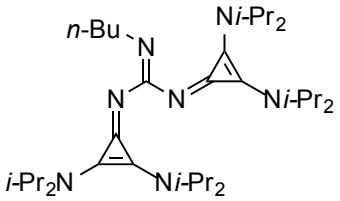
Second filtration performed using pentane instead of PhMe. Pale yellow syrup (30 mg, 96%, 0.1 mmol scale). ^{1}H NMR (500 MHz, CD_3CN) δ 2.98 (t, J = 6.9 Hz, 2H), 2.70 (d, J = 8.8 Hz, 24H), 1.44 (m, 2H), 1.37 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H).

GP_2 (10)



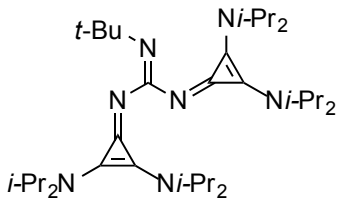
White solid (66 mg, 97%, 0.1 mmol scale). ^{1}H NMR (300 MHz, d_8-PhMe) δ 3.67 (t, J = 6.8 Hz, 2H), 3.17 (m, 24H), 1.83 (m, 2H), 1.71 (m, 2H), 1.48 (br s, 36H), 1.14 (t, J = 7.3 Hz, 3H). ^{31}P NMR (121 MHz, d_8-PhMe) δ 24.19, 11.11.

GC_2 (6)



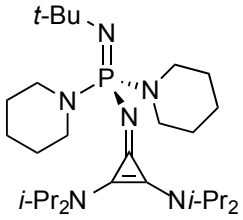
White semisolid (53 mg, 91%, 0.1 mmol scale). ^{1}H NMR (300 MHz, d_8-PhMe) δ 4.07 (br app quint, J = 6.8 Hz, 4H), 3.85 (t, J = 7.2 Hz, 2H), 3.67 (br app quint, J = 6.8 Hz, 4H), 1.89 (m, 2H), 1.68 (hex, J = 7.3 Hz, 2H), 1.23 – 1.02 (overlapping signals, 50H).

GC_2 (8)



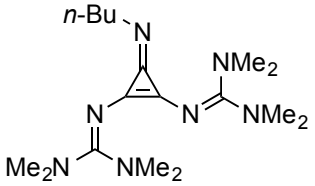
White semisolid (578 mg, 99%, 1 mmol scale). ^{1}H NMR (300 MHz, d_8-PhMe) δ 4.18 (br m, 4H), 3.70 (br m, 4H), 1.80 (s, 9H), 1.13 (br m, 48H).

PC_1 (14)



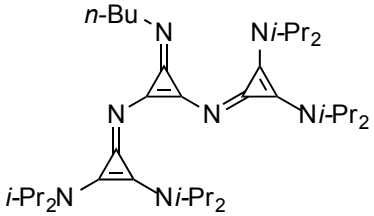
White solid (49 mg, 94%, 0.1 mmol scale). ^{1}H NMR (300 MHz, d_8-PhMe) δ 3.88 (hept, J = 6.8 Hz, 4H), 3.43 (m, 8H), 1.56 (br s, 12H), 1.53 (d, J = 1.1 Hz, 9H), 1.13 (d, J = 6.7 Hz, 24H). ^{31}P NMR (121 MHz, d_8-PhMe) δ 4.68.

CG_2 (4)



Liberated at -20 °C.Pale yellow syrup (31 mg, 92%, 0.1 mmol scale). ^{1}H NMR (300 MHz, d_8-PhMe) δ 3.63 (t, J = 6.7 Hz, 2H), 2.65 (s, 12H), 2.53 (s, 12H), 1.85 (m, 2H), 1.65 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H).

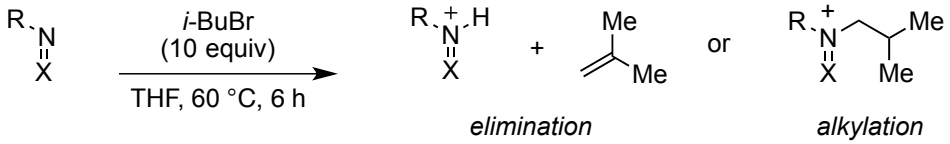
C_3 (2)



Yellow-orange solid (54 mg, 89%, 0.1 mmol scale). ^{1}H NMR (300 MHz, d_8-PhMe) δ 3.96 (quint, J = 6.7 Hz, 4H), 3.84 (t, J = 6.7 Hz, 2H), 3.60 (quint, J = 6.3 Hz, 4H), 1.89 (quint, J = 6.8 Hz, 2H), 1.70 (m, 7.2 Hz, 2H), 1.20 – 1.06 (overlapping signals, 51H).

Alkylation Studies on Higher-Order Superbases

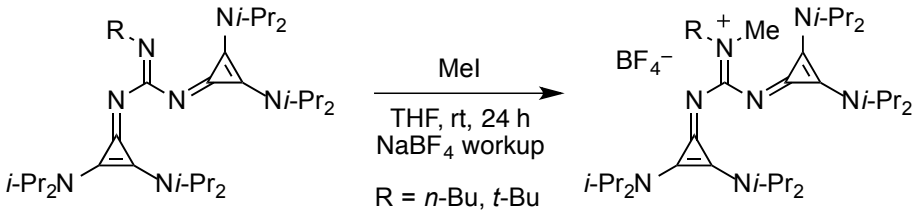
Alkylation vs. Elimination Selectivity with *iso*-butyl bromide



A solution of KO*t*-Bu (1 M in *t*-BuOH, 0.10 mL, 0.10 mmol, 1.0 equiv) was added to a solution of higher-order superbase conjugate acid salt (0.10 mmol, 1.0 equiv) in THF (0.5 mL). After 10 minutes, 1-bromo-2-methylpropane (0.11 mL, 1.0 mmol, 10 equiv) was added, and the reaction was heated at 60 °C for 6 hours. After cooling to room temperature, the reaction was quenched with a combination of 0.2 M $NaBF_4$ and 10% sat. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (2 x 10 mL), dried over Na_2SO_4 and concentrated. The crude mixture was analyzed by ^1H NMR spectroscopy and mass spectrometry. The alkylation/elimination ratio was determined by the relative amounts of the alkylated and protonated superbases in the spectrum, and where alkylation occurred to an appreciable (> 5%) extent, the cation was identified by LRMS.

superbase class	G_3	GP_2	Bu-GC_2	*t*-Bu-GC_2	CG_2	C_3
compound number	**11**	**10**	**6**	**8**	**4**	**2**
signals integrated (alkylation)	C**H₂**Pr C**H₂***i*-Pr	C**H**Me₂	C**H₂***i*-Pr	C**H₂***i*-Pr	C**H₂***i*-Pr	C**H₂**Pr C**H₂***i*-Pr
cation formula	$C_{19}H_{42}N_7^+$	$C_{39}H_{78}N_9P_2^+$	$C_{39}H_{74}N_7^+$	$C_{39}H_{74}N_7^+$	$C_{21}H_{42}N_7^+$	$C_{41}H_{74}N_7^+$
LRMS calc'd	368.35	734.59	640.60	640.60	392.35	664.60
LRMS found	368.34	nd	640.67	nd	392.30	664.65
signals integrated (elimination)	N**H** C**H₂**Pr	N**H**	N**H**	N**H**	N**H**	N**H** C**H₂**Pr
alkylation/ elimination	67:33	3.0:97.0	31:69	2.8:97.2	78:22	57:43

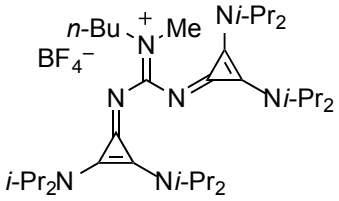
Methylation of GC_2 Superbases



A solution of KO*t*-Bu (1 M in *t*-BuOH, 0.080 mL, 0.080 mmol, 1.0 equiv) was added to a

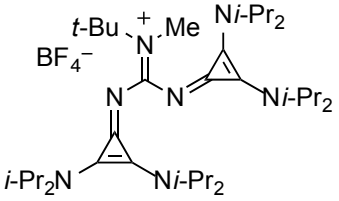
solution of GC_2•HBF_4 (54 mg, 0.080 mmol, 1.0 equiv) in THF (0.55 mL) After 10 minutes, iodomethane (10 µL, 0.16 mmol, 2.0 equiv) was added, and the reaction was stirred for 24 hours. It was then quenched with a combination of 0.2 M $NaBF_4$ and 10% sat. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (2 x 10 mL), dried over Na_2SO_4 and concentrated.

Bis(2,3-bis(diisopropylamino)cyclopropeniminyl)-*N*-butyl-*N*-methyliminium tetrafluoroborate (S6)



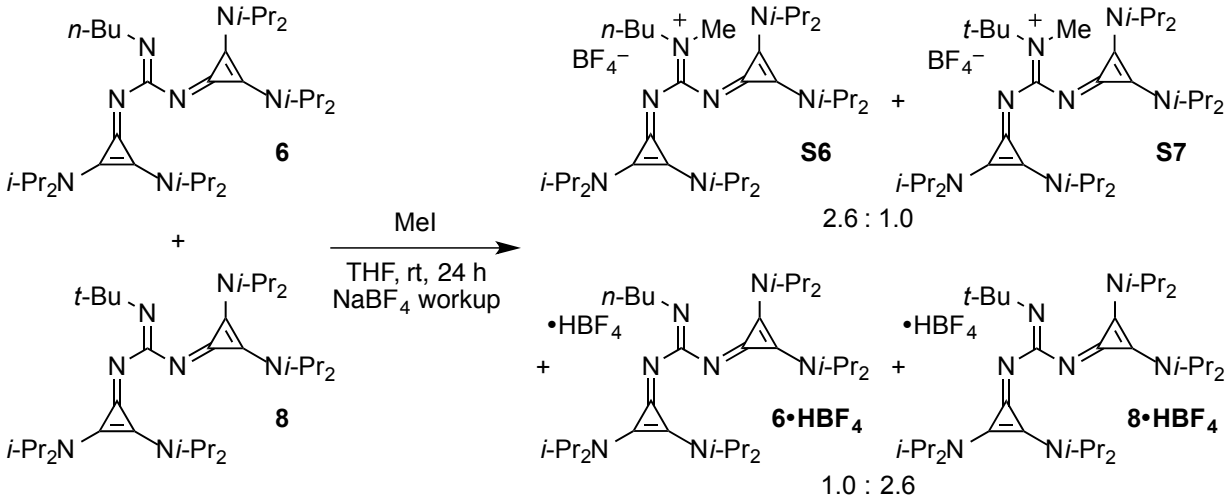
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (hept, J = 6.8 Hz, 8H), 3.28 (app t, 2H), 2.91 (s, 3H), 1.58 (m, 2H), 1.35 – 1.20 (overlapping signals, 50H), 0.90 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.20, 120.92, 120.08, 51.59, 50.25, 36.97, 28.96, 22.18, 20.21, 14.04. LRMS (APCI+) for $C_{36}H_{68}N_7^+$ m/z calcd 598.55, found 598.66.

Bis(2,3-bis(diisopropylamino)cyclopropeniminyl)-*N*-*tert*-butyl-*N*-methyliminium tetrafluoroborate (S7)



~3.5:1 mixture with **8**•HBF_4. ^{1}H NMR (400 MHz, $CDCl_3$) after subtracting contributions from **8**•HBF_4 δ 3.85 (hept, J = 6.8 Hz, 8H), 2.76 (s, 3H), 1.44 (s, 9H), 1.27 (d, J = 6.8 Hz, 48H). ^{13}C NMR (101 MHz, $CDCl_3$) after subtracting contributions from **8**•HBF_4 δ 165.4, 120.8, 120.6, 56.8, 50.2, 35.7, 28.0, 22.1. LRMS (APCI+) for $C_{36}H_{68}N_7^+$ m/z calcd 598.55, found 598.69.

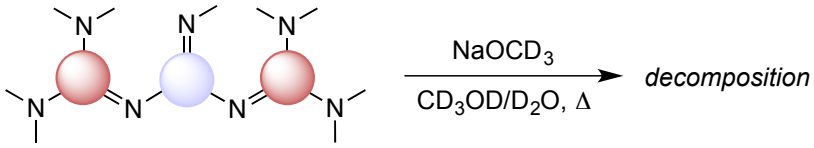
Concurrent Methylation of GC_2 Superbases



A solution of KO*t*-Bu (1 M in *t*-BuOH, 0.30 mL, 0.30 mmol, 2.0 equiv) was added to a solution of **6**•HBF_4 (101 mg, 0.150 mmol, 1.0 equiv) and **8**•HBF_4 (101 mg, 0.150 mmol, 1.0 equiv) in THF (1.5 mL) at 0 °C. After warming to room temperature over 10 minutes, iodomethane (9.25 µL, 0.149 mmol, 1.0 equiv) was added, and the reaction was stirred for 24 hours. It was then

quenched with a combination of 0.2 M $NaBF_4$ and 10% sat. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (2 x 10 mL), dried over Na_2SO_4 and concentrated. ^1H NMR analysis showed a 2.6:1.0 mixture of methylated compounds **S6** and **S7** (by integrating N-CH_3 signals) and a 1.0:2.6 mixture of protonated compounds **6**•HBF_4 and **8**•HBF_4 (by integrating N-H signals).

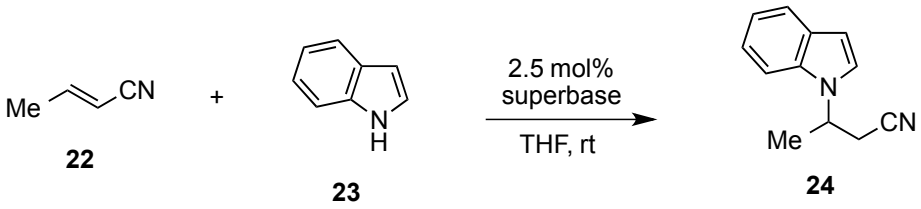
Hydrolytic Stabilities of Higher-Order Superbases



A solution $NaOCD_3$ (5.0M, prepared by adding freshly cut sodium to CD_3OD, 0.15 mL, 0.75 mmol, 10 equiv) was added to a solution of higher-order superbase conjugate acid salt (0.075 mmol, 1.0 equiv) and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (internal standard, 10 mg, 0.046 mmol, 0.6 equiv) in CD_3OD (0.30 mL) at room temperature. After stirring for 10 minutes, D_2O (0.25 mL) was added, and the solution was transferred to an NMR tube. Reactions were monitored by ^1H NMR spectroscopy until the starting superbase contained about 50% of its initial concentration compared to the internal standard. Reactions at 140 °C were flame-sealed in their NMR tubes prior to heating.

superbase class	compd. number	signal integrated	temp. (°C)	time	% intact	$t_{1/2}$ rel.	pK_{BH+}
G_1	**16**	$N(C\mathbf{H_3})_2$	80	40 m	49	2.7	24.8
P_1	**18**	all	140	24 h	100	$> 10^4$	27.8
C_1	**17**	$NC\mathbf{H}Me_2$	80	1 h	48	4.0	27.6
G_3	**11**	$NC\mathbf{H_2}$	80	2 h	50	8.0	29.5
GP_2	**10**	all	140	24 h	100	$> 10^4$	34.3
GC_2	**6**	$NC\mathbf{H}Me_2$	140	2.25 h	50	81	35.6
PG_3	**19**	$N(C\mathbf{H_3})_2$	140	32 h	50	1200	37.9
PC_1	**14**	all	140	24 h	100	$> 10^4$	31.8
CG_2	**4**	$N(C\mathbf{H_3})_2$	80	15 m	50	1.0	29.0
C_3	**2**	$NC\mathbf{H_2}$	80	9 h	50	36	31.6
C_3	**2**	$NC\mathbf{H_2}$	140	1 h	49	36	31.6

Catalytic Activities of C_1 Base 17 and C_3 Base 2, and *t*-Bu-GC_2 Base 8



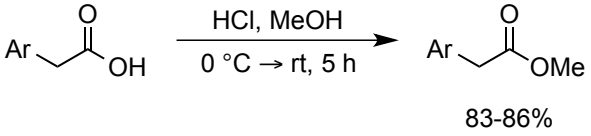
A solution of KO*t*-Bu (1 M in *t*-BuOH of THF, 25 µL, 0.025 mmol, 0.025 equiv) was added to a solution of superbase HBF_4 salt (0.030 mmol, 0.030 equiv) in THF (2 mL), followed by indole (176 mg, 1.50 mmol, 1.50 equiv) in THF (1 mL) and crotonitrile (mixture of *cis* and *trans*, 81.5 µL, 1.00 mmol, 1.00 equiv). After stirring for 3-24 hours, the reaction was diluted with diethyl ether (100 mL), washed with 50% sat. NH_4Cl (2 x 50 mL) and brine (25 mL), dried over Na_2SO_4, and concentrated. The orange residue was purified by chromatography (5 % EtOAc/hexanes → 20%) on silica gel (40 mL) to afford the desired adduct[11] as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.23 (m, 1H), 7.20 (d, *J* = 3.3 Hz, 1H), 7.13 (m, 1H), 6.56 (d, *J* = 3.3 Hz, 1H), 4.80 (m, 1H), 2.71 (m, 2H), 1.72 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.4, 128.9, 123.4, 122.1, 121.5, 120.2, 116.9, 108.9, 103.0, 47.6, 25.4, 19.5. LRMS (APCI+) for $C_{12}H_{12}N_2$ $[MH]^+$ m/z calcd 185.11 found 185.18.

C_1 base **17** gave 0% conversion to the desired adduct after 24 hours.

C_3 base **2** gave 92% conversion to the desired adduct after 3 hours, and the product was isolated (164 mg, 89%).

t-Bu-GC_2 base **8** gave 97% conversion to the desired adduct after 3 hours, and the product was isolated (175 mg, 95%).

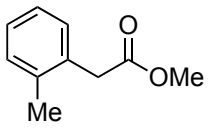
Preparation of α-Aryl Esters



Acetyl chloride (1.3 mL, 18 mmol, 1.2 equiv) was added dropwise to a solution of α-aryl acid (15 mmol, 1.0 equiv) in MeOH (45 mL) at 0 °C. The reaction was warmed to room temperature over 5 hours, then quenched with sat. $NaHCO_3$ (50 mL), extracted with CH_2Cl_2 (3 x 50 mL), dried over Na_2SO_4, and concentrated. The resulting liquids were distilled at reduced pressure.

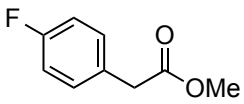
11. Sunaba, H.; Kamata, K.; Mizuno, N. *ChemCatChem* **2014**, *6*, 2333.

Methyl (2-methylphenyl)acetate



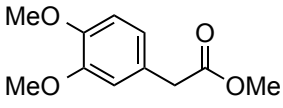
Clear, colorless liquid (2.08 g, 85%). bp 56-57 °C/~ 1 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (br s, 4H), 3.68 (s, 3H), 3.64 (s, 2H), 2.31 (s, 3H).

Methyl (4-fluorophenyl)acetate



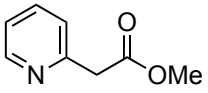
Clear, colorless liquid (2.10 g, 83%). bp 53-55 °C/~ 1 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24(m, 2H), 7.01 (m, 2H), 3.69 (s, 3H), 3.60 (s, 2H).

Methyl (3,4-dimethoxyphenyl)acetate



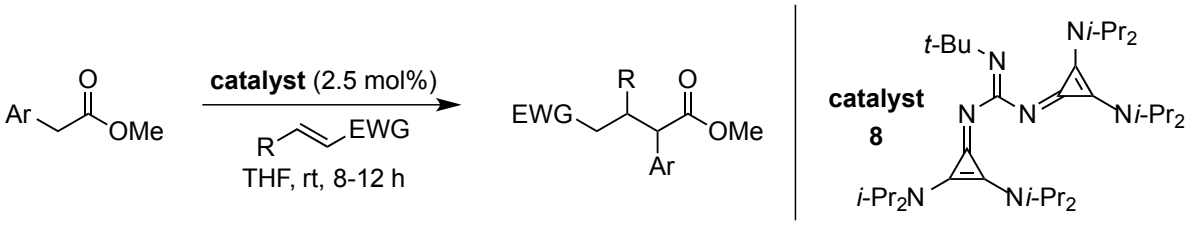
Clear, colorless liquid (2.69 g, 85%). bp 150-165 °C/~ 1 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 3.69 (s, 3H), 3.56 (s, 2H).

Methyl 2-pyridylacetate



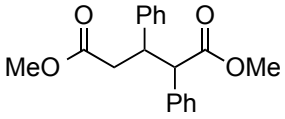
Prepared from the HCl salt of 2-pyridylacetic acid. Clear, yellow-green liquid (1.95 g, 86%). bp 62-64 °C/~ 1 mmHg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, J = 4.3 Hz, 1H), 7.66 (td, J = 7.7, 1.9 Hz, 1H), 7.29 (m, 1H), 7.19 (m, 1H), 3.86 (s, 2H), 3.73 (s, 3H).

Conjugate Additions of α-Aryl Esters and Nitriles



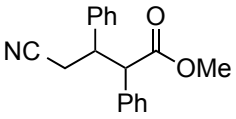
A solution of KO*t*-Bu (1 M in *t*-BuOH of THF, 25 μL, 0.025 mmol, 0.025 equiv) was added to a solution of **8**•HBF_4 (20.3 mg, 0.0302 mmol, 0.030 equiv) in THF (3 mL), followed by the α-aryl ester or nitrile and Michael acceptor (1 mmol scale, see below for details, ratios were typically selected to simplify purification). After stirring for 8-12 hours, acetic acid was added (2 drops), and the reaction was concentrated. The residue was purified by chromatography (EtOAc/hexanes) on silica gel (40 mL) to afford the desired adducts.

Dimethyl 2,3-diphenylglutarate (25)[12]



White solid (296 mg, 95%). Crude dr 53:47 *syn*/*anti*. ^{1}H NMR (500 MHz, $CDCl_3$) ~5:4 mixture is diastereomers, δ 7.47 (app d, J = 6.9 Hz, 1H), 7.37 – 7.17 (m, 4H), 7.14 – 6.96 (m, 5H), 3.87 (m, 2H), 3.66 (s, 1.65H, $3H_{syn}$), 3.49 (s, 1.65H, $3H_{syn}$), 3.37 (s, 1.35H, $3H_{anti}$), 3.34 (s, 1.35H, $3H_{anti}$), 2.81 (m, 1H), 2.41 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.40, 172.7, 172.00, 171.9, 141.3, 140.3, 136.7, 136.6, 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 128.00, 127.30, 127.2, 126.7, 57.8, 57.2, 52.2, 51.8, 51.6, 51.4, 45.6, 45.3, 39.3, 38.7. LRMS (APCI+) for $C_{19}H_{20}O_4$ $[MH]^+$ m/z calcd 313.14 found 313.12.

Methyl 4-cyano-2,3-diphenylbutyrate (26)

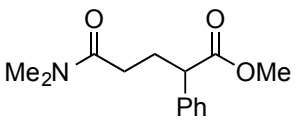


White solid (278 mg, 100%). Crude dr 64:36 *anti*/*syn*.[13] ^{1}H NMR (500 MHz, $CDCl_3$) ~2:1 mixture is diastereomers, δ 7.52 – 7.06 (m, 10H), 4.07 (d, J = 11.7 Hz, 0.66H, $1H_{anti}$), 3.95 (s, 0.33H, $1H_{syn}$), 3.73 – 3.64 (overlapping signals, 2H), 3.42 (s, 2H, $3H_{anti}$), 2.91 (dd, J = 16.8, 8.5 Hz, 0.33 H, $1H_{syn}$), 2.80 (dd, J = 16.8, 4.2 Hz, 0.33H, $1H_{syn}$), 2.40 (dd, J = 16.8, 3.8 Hz, 0.66H, $1H_{anti}$), 2.30 (dd, J = 16.8, 8.1 Hz, 0.66H, $1H_{anti}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 172.1, 139.5, 138.4, 136.0, 135.8, 129.4, 129.0, 128.7, 128.61, 128.58, 128.5, 128.4, 128.1, 128.0, 127.69, 127.65, 118.0, 117.8, 55.9, 55.7, 52.6, 52.1, 45.02, 44.99, 23.3, 23.0. LRMS (APCI+) for $C_{18}H_{17}NO_2$ $[MH]^+$ m/z calcd 280.13 found 280.12.

Using the isolated free base **8** (2.5 mol%) as the catalyst (aprotic conditions), the product was obtained in 99% yield and 66:34 *anti*/*syn* crude dr.

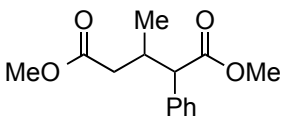
Using the P_4-*t*Bu phosphazene **21** (2.5 mol%) as a catalyst under aprotic conditions, the product was obtained in 59% yield and 54:46 *anti*/*syn* crude dr.

Methyl 4-(*N*,*N*-dimethylcarbamoyl)-2-phenylbutyrate (27)



Pale yellow oil (207 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 5H), 3.71 (t, J = 7.7 Hz, 1H), 3.65 (s, 3H), 2.92 (s, 3H), 2.89 (s, 3H), 2.39 (m, 1H), 2.26 (m, 2H), 2.12 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.3, 172.0, 138.8, 128.7, 128.0, 127.4, 52.0, 50.6, 37.1, 35.4, 30.8, 28.7. LRMS (APCI+) for $C_{14}H_{19}NO_3$ $[MH]^+$ m/z calcd 250.14 found 250.14.

Dimethyl 3-methyl-2-phenylglutarate (28)[14]

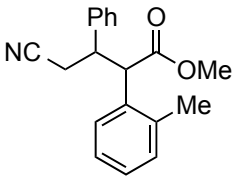


Pale yellow oil (248 mg, 100%). Crude dr 61:39 *syn*/*anti*. ^{1}H NMR (500 MHz, $CDCl_3$) ~3:2 mixture is diastereomers, δ 7.43 – 7.15 (m, 5H),

12. Smith, S. R.; Leckie, S. M.; Holmes, R.; Douglas, J.; Fallan, C.; Shapland, P.; Pryde, D.; Slawin, A. M. Z.; Smith, A. D. *Org. Lett.* **2014**, *16*, 2506.
13. For the ethyl ester: Poncele, M.; Bulachz, C.; Simonz, P. *Eur. J. Med. Chem.* **1990**, *25*, 641.
14. Gospodova, T. S.; Stefanovsky, Y. N. *Monatshefte für Chemie* **1989**, *125*, 217.

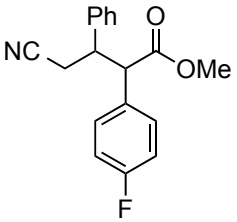
3.68 (s, 1.8H, 3H$_{syn}$), 3.65 (s, 1.2H, 3H$_{anti}$), 3.64 (s, 1.8H, 3H$_{syn}$), 3.57 (s, 1.2H, 3H$_{anti}$), 3.43 (d, J = 10.0 Hz, 0.6H, 1H$_{syn}$), 3.40 (d, J = 10.6 Hz, 0.4H, 1H$_{anti}$), 2.72 (m, 1H), 2.49 (dd, J = 15.2, 4.2 Hz, 0.6H, 1H$_{syn}$), 2.26 (dd, J = 15.2, 9.0 Hz, 0.6H, 1H$_{syn}$), 2.17 (dd, J = 15.5, 4.0 Hz, 0.4H, 1H$_{anti}$), 1.92 (dd, J = 15.5, 9.3 Hz, 0.4H, 1H$_{anti}$), 1.08 (d, J = 6.5 Hz, 1.2H, 3H$_{anti}$), 0.79 (d, J = 6.8 Hz, 1.8H, 3H$_{syn}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 172.9, 172.8, 137.31, 137.25, 128.8, 128.7, 128.6, 127.7, 127.6, 57.7, 57.2, 51.97, 51.95, 51.6, 51.4, 39.5, 38.5, 33.8, 33.5, 18.6, 17.4. LRMS (APCI+) for $C_{14}H_{18}O_4$ $[MH]^+$ m/z calcd 251.13 found 251.12.

Methyl 4-cyano-2-(2-methylphenyl)-3-phenylbutyrate (29)



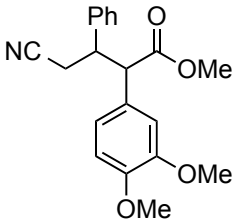
White solid (240 mg, 82%). Crude dr 63:37 *anti*/*syn*.[15] ^{1}H NMR (500 MHz, $CDCl_3$) ~7:3 mixture is diastereomers, δ 7.53 (d, J = 7.5 Hz, 0.64H, 1H$_{anti}$), 7.45 – 7.05 (m, 7.64H), 7.02 (t, J = 7.4 Hz, 0.36H, 1H$_{syn}$), 6.96 (d, J = 7.6 Hz, 0.36H, 1H$_{syn}$), 4.42 (d, J = 11.7 Hz, 0.64H, 1H$_{anti}$), 4.29 (d, J = 10.9 Hz, 0.36H, 1H$_{syn}$), 3.84 – 3.71 (overlapping signals, 1H), 3.68 (s, 1.08H, 3H$_{syn}$), 3.40 (s, 1.92H, 3H$_{anti}$), 2.98 (dd, J = 16.8, 8.8 Hz, 0.36H, 1H$_{syn}$), 2.87 (m, 0.36H, 1H$_{syn}$), 2.55 (s, s, 1.92H, 3H$_{anti}$), 2.39 (m, 1.28H, 2H$_{anti}$), 2.20 (s, 1.08H, 3H$_{syn}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 172.4, 139.6, 138.6, 137.5, 136.5, 134.6, 134.1, 131.3, 130.7, 129.1, 128.6, 128.2, 128.1, 127.8, 127.74, 127.72, 127.6, 127.18, 127.15, 126.7, 126.4, 118.2, 52.6, 52.2, 50.6, 50.4, 44.9, 44.6, 23.1, 22.5, 20.2, 19.9. LRMS (APCI+) for $C_{19}H_{19}NO_2$ $[MH]^+$ m/z calcd 294.15 found 293.61.

Methyl 4-cyano-2-(4-fluorophenyl)-3-phenylbutyrate (30)



White solid (296 mg, 100%). Crude dr 64:36 *anti*/*syn*.[15] ^{1}H NMR (500 MHz, $CDCl_3$) ~8:5 mixture is diastereomers, δ 7.48 (dd, J = 8.2, 5.3 Hz, 1.24H, 2H$_{anti}$), 7.43 – 7.02 (m, 18H), 6.83 (t, J = 8.4 Hz, 0.76H, 2H$_{syn}$), 4.08 (d, J = 11.8 Hz, 0.62H, 1H$_{anti}$), 3.99 (d, J = 11.1 Hz, 0.38H, 1H$_{syn}$), 3.71 (s, 1.14H, 3H$_{syn}$), 3.65 (m, 1H), 3.40 (s, 1.86H, 3H$_{anti}$), 2.87 (dd, J = 16.8, 8.3 Hz, 0.38H, 1H$_{syn}$), 2.78 (dd, J = 16.9, 4.3 Hz, 0.38H, 1H$_{syn}$), 2.40 (dd, J = 16.9, 3.8 Hz, 0.62H, 1H$_{anti}$), 2.31 (dd, J = 16.8, 7.9 Hz, 0.62H, 1H$_{anti}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 172.0, 163.8, 163.1, 161.8, 161.1, 139.2, 138.2, 131.74, 131.71, 131.52, 131.49, 130.14, 130.07, 130.0, 129.1, 128.8, 128.2, 127.9, 127.8, 127.6, 117.9, 117.7, 116.4, 116.3, 115.6, 115.4, 54.94, 54.87, 52.7, 52.2, 45.03, 44.99, 23.40, 22.9. LRMS (APCI+) for $C_{18}H_{16}FNO_2$ $[MH]^+$ m/z calcd 298.12 found 297.58.

Methyl 4-cyano-2-(3,4-dimethoxyphenyl)-3-phenylbutyrate (31)

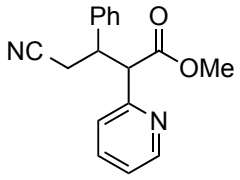


White solid (335 mg, 99%). Crude dr 64:36 *anti*/*syn*.[15] ^{1}H NMR (500 MHz, $CDCl_3$) ~7:3 mixture is diastereomers, δ 7.38 (m, 2.7H, 3H$_{anti}$ and 2H$_{syn}$), 7.29 (t, J = 7.3 Hz, 0.7H, 1H$_{anti}$), 7.15 (m, 1H), 7.07 (d, J = 7.5 Hz, 0.6H, 2H$_{syn}$), 7.02 (m, 1.4H, 2H$_{anti}$), 6.88 (d, J = 8.1 Hz, 0.7H, 1H$_{anti}$), 6.65 (m, 0.6, 2H$_{syn}$), 6.55 (s, 0.3, 1H$_{syn}$), 4.02 (d, J = 11.7 Hz, 0.7H, 1H$_{anti}$), 3.92 (overlapping signals, 2.4H, 3H$_{anti}$ and 1H$_{syn}$), 3.88 (s, 2.1H, 3H$_{anti}$), 3.75 (s,

15. Assigned in analogy to methyl 4-cyano-2,3-diphenylbutyrate (**26**).

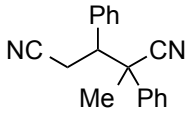
0.9H, 3H$_{syn}$), 3.71 (2 x overlapping s, 1.8H, 6H$_{syn}$), 3.63 (m, 1H), 3.41 (s, 2.1H, 3H$_{anti}$), 2.86 (dd, J = 16.8, 8.4 Hz, 0.3, 1H$_{syn}$), 2.78 (dd, J = 16.8, 4.4 Hz, 0.3, 1H$_{syn}$), 2.42 (dd, J = 16.8, 3.7 Hz, 0.7H, 1H$_{anti}$), 2.32 (dd, J = 16.8, 7.9 Hz, 0.7H, 1H$_{anti}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 172.2, 149.4, 149.1, 148.6, 148.2, 139.4, 138.4, 128.9, 128.6, 128.1, 128.0, 127.93, 127.86, 127.54, 127.50, 120.7, 120.6, 118.0, 117.9, 111.5, 111.4, 110.78, 110.76, 56.0, 55.9, 55.7, 55.6, 55.1, 52.5, 52.0, 44.94, 44.91, 23.1, 22.8. LRMS (APCI+) for $C_{20}H_{21}NO_2$ $[MH]^+$ m/z calcd 340.15 found 339.55.

Methyl 4-cyano-2-(2-pyridyl)-3-phenylbutyrate (32)



Tan solid (276 mg, 99%). Crude dr 64:36 *anti*/*syn*.[15] ^{1}H NMR (500 MHz, $CDCl_3$) ~2:1 mixture is diastereomers, δ 8.67 (d, J = 4.8 Hz, 0.66H, 1H$_{anti}$), 8.46 (d, J = 4.8 Hz, 0.34H, 1H$_{syn}$), 7.74 (t, J = 7.5 Hz, 0.66H, 1H$_{anti}$), 7.49 (d, J = 7.8 Hz, 0.66H, 1H$_{anti}$), 7.39 (m, 3H), 7.30 (m, 1.34H), 7.17 (m, 1.66H), 7.03 (m, 0.34H, 1H$_{syn}$), 6.99 (d, J = 7.9 Hz, 0.34H, 1H$_{syn}$), 4.33 (d, J = 11.4 Hz, 0.66H, 1H$_{anti}$), 4.25 (d, J = 10.7 Hz, 0.34H, 1H$_{syn}$), 4.03 (m, 0.66H, 1H$_{anti}$), 3.97 (m, 0.34H, 1H$_{syn}$), 3.72 (s, 1H, 3H$_{syn}$), 3.44 (s, 2H, 3H$_{anti}$), 3.02 (dd, J = 16.8, 8.6 Hz, 0.34H, 1H$_{syn}$), 2.90 (dd, J = 16.9, 3.9 Hz, 0.34H, 1H$_{syn}$), 2.47 (m, 1.32H, 2H$_{anti}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.75, 170.84, 155.85, 155.23, 150.26, 149.61, 139.49, 138.67, 137.4, 136.6, 129.0, 128.7, 128.0, 127.9, 127.7, 127.6, 124.3, 124.0, 123.3, 122.5, 118.2, 117.9, 57.8, 57.5, 52.7, 52.3, 43.6, 43.2, 23.1, 22.7. LRMS (APCI+) for $C_{17}H_{16}N_2O_2$ $[MH]^+$ m/z calcd 281.13 found 280.62.

2-Methyl-2,3-diphenylglutaronitrile (33)



Tan solid (250 mg, 96%). Crude dr 71:29. ^{1}H NMR (500 MHz, $CDCl_3$) ~7:3 mixture is diastereomers, δ 7.55 (d, J = 7.8 Hz, 1.4H, 2H$_{major}$), 7.50 – 7.37 (m, 6H), 7.27 – 7.16 (m, 1.4H, 2H$_{major}$), 7.14 (m, 0.6H, 2H$_{minor}$), 6.92 (d, J = 7.5 Hz, 0.6H, 2H$_{minor}$), 3.41 (dd, J = 11.3, 4.7 Hz, 0.3H, 1H$_{minor}$), 3.32 (dd, J = 12.1, 3.9 Hz, 0.7H, 1H$_{major}$), 3.06 (dd, J = 16.8, 4.7 Hz, 0.3H, 1H$_{minor}$), 2.90 (overlapping signals, 1H), 2.45 (dd, J = 16.8, 3.9 Hz, 0.7H, 1H$_{major}$), 1.84 (s, 0.9H, 3H$_{minor}$), 1.48 (s, 2.1H, 3H$_{major}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 136.7, 135.7, 135.3, 129.6, 129.2, 129.1, 128.91, 128.85, 128.73, 128.71, 128.6, 128.5, 128.4, 126.5, 125.6, 121.8, 120.8, 117.7, 117.5, 52.2, 51.9, 47.3, 46.7, 26.8, 24.9, 20.8, 20.5. LRMS (ESI+) for $C_{18}H_{16}N_2$ $[MNa]^+$ m/z calcd 283.12 found 283.14.

X-Ray Crystallographic Studies

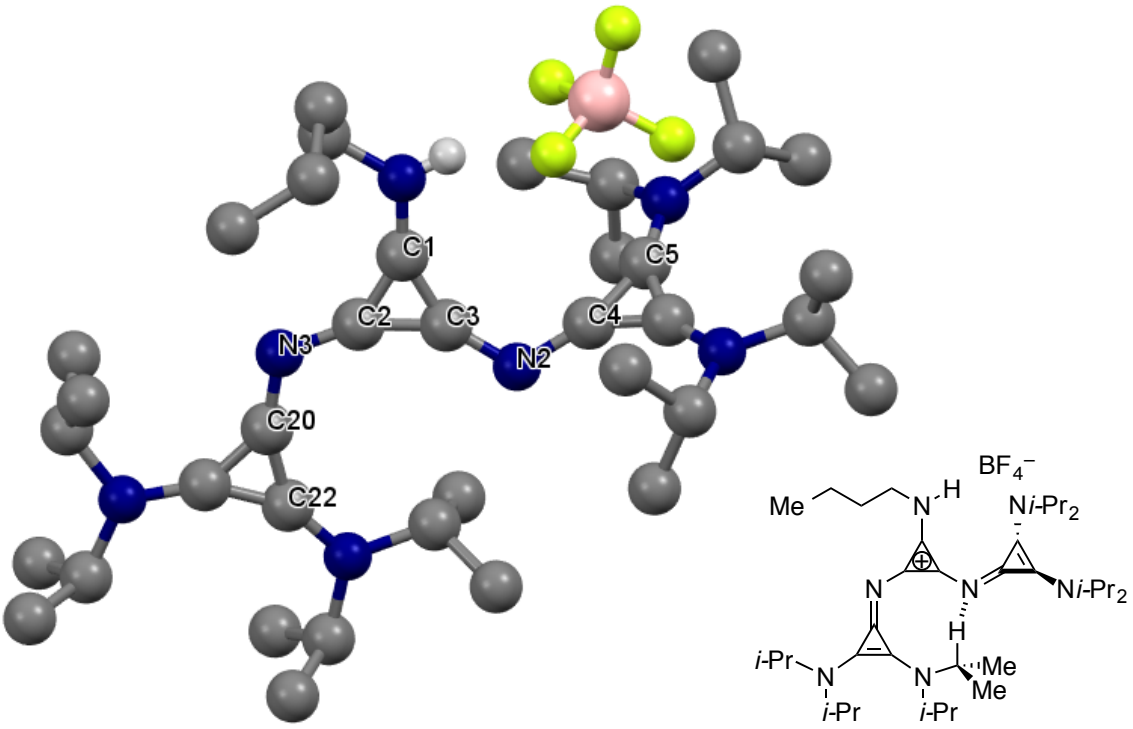


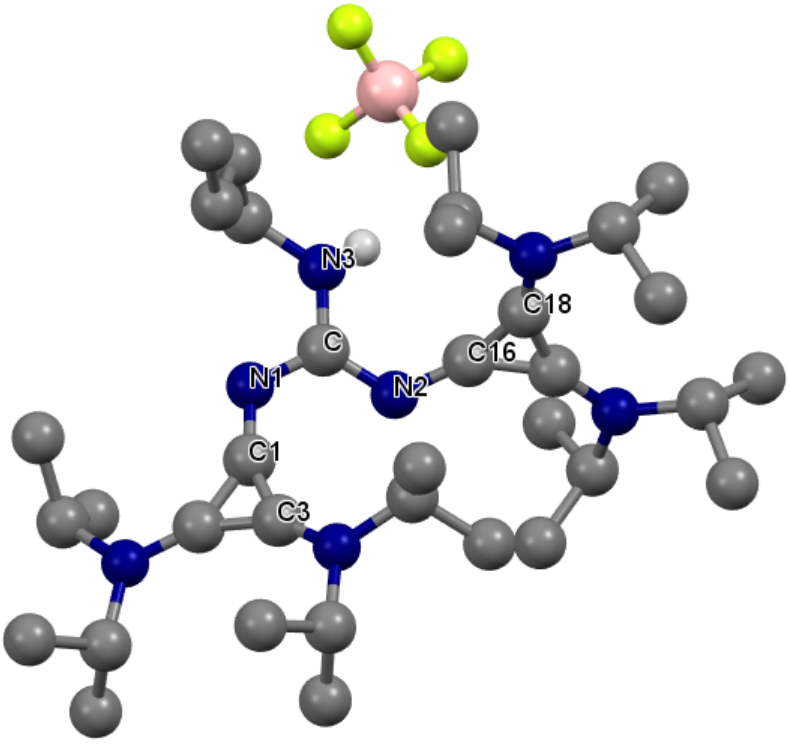
Figure S2. Crystal structure of **2**•HBF_4. **2•HBF_4**

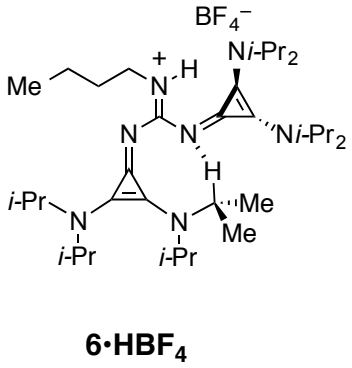
Both cyclopropenimine substituents are tilted from the plane of the central ring:
left substituent: 2.7° below (N3-C2-C1-C3 dihedral angle), 7.8° below (C3-C2-N3-C20)
right substituent: 9.2° above (N2-C3-C1-C2 dihedral angle), 17.9° below (C1-C3-N2-C4)

These substituents are also twisted to various degrees from this plane:
left substituent: 2.1° (C2-N3-C20-C22 dihedral angle)
right substituent: 65.6° (C3-N2-C4-C5 dihedral angle)

The substituents deviate slightly from ideal 120° angles to the ring:
left substituent: 119.4° (C2-N3-C20 angle)
right substituent: 117.6° (C3-N2-C4 angle)

Crystal growth method. The salt (150 mg) was dissolved in hot EtOAc (3 mL) and cooled to room temperature over 1 hour. Hexanes was diffused into this loose-capped vial by standing in sealed jar containing a layer of hexanes. After 3 days, large colorless crystals had formed and were submitted for analysis.





6·HBF$_4$

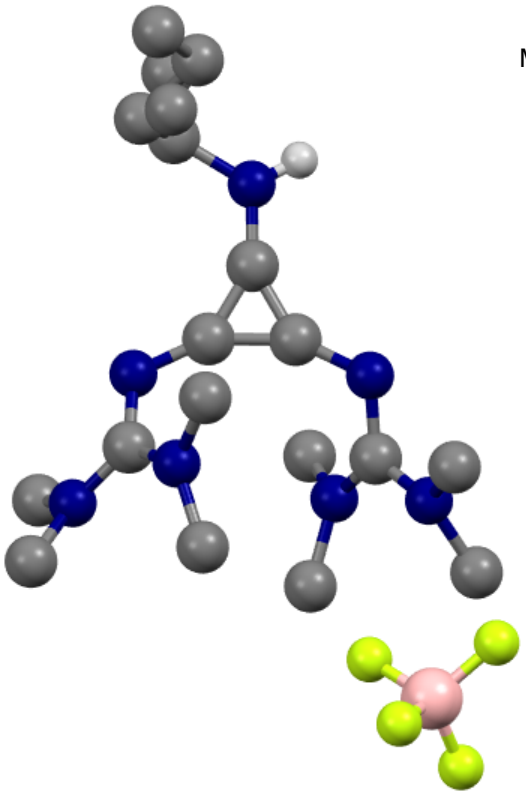
Figure S3. Crystal structure of **6**•HBF$_4$.

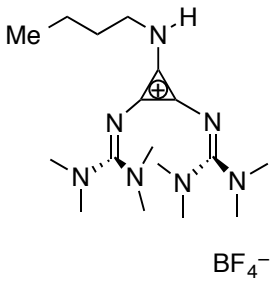
Both cyclopropenimine substituents are tilted above the plane of the central guanidinium system:
left substituent: 22.9° (N2-C-N1-C1 dihedral angle)
right substituent: 32.9° (N3-C-N2-C16 dihedral angle)

These substituents are also twisted somewhat from this plane:
left substituent: 35.1° (C-N1-C1-C3 dihedral angle)
right substituent: 45.1° (C-N2-C16-C18 dihedral angle)

The substituents deviate slightly from ideal 120° angles to the guanidinium system:
left substituent: 119.0° (C-N1-C1 angle)
right substituent: 121.7° (C-N2-C16 angle)

Crystal growth method. The salt (150 mg) was dissolved in hot EtOAc (3 mL) and cooled to room temperature over 1 hour. Hexanes was diffused into this loose-capped vial by standing in sealed jar containing a layer of hexanes. After 2 days, small colorless crystals had formed and were submitted for analysis.





4•HBF$_4$

Figure S4. Crystal structure of the more ordered ion pair of **4**•HBF$_4$.

This structure contains two distinct ion pairs, pictured below. The image above, also shown in the manuscript, is from viewing the structure on the left from the perspective indicated.

There is also significant disorder in the structure. The left cation's butyl group is disordered, as are the front BF_4 anion, and the butyl and imino groups of the right cation.

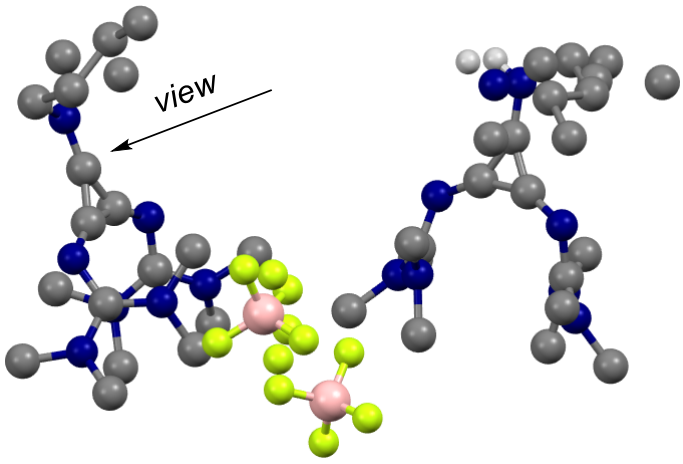
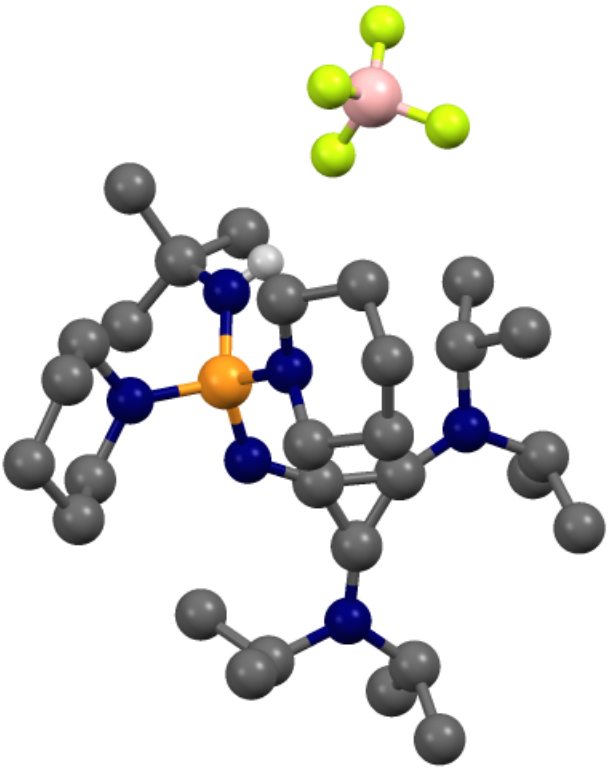
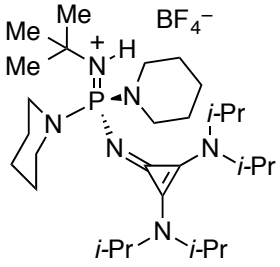


Figure S5. Crystal structure of both ion pairs of **4**•HBF$_4$.

Crystal growth method. The salt (100 mg) was dissolved in hot EtOAc (3 mL) and cooled to

room temperature overnight. A few small grains (3-5) were added for seeding. After standing in the sealed vial for 1 day, hexanes was diffused into this vial by slightly loosening the cap and by standing in sealed jar containing a layer of hexanes. After 5 days, small pale yellow crystals had formed and were submitted for analysis. Note: this material oiled out easily; the seeding, the standing period before diffusing in hexanes, and the slower diffusion enforced by the relatively tight cap were all essential in forming crystals instead of an oil. Furthermore, the solid material not used for the analysis turned into an oil after prolonged standing in solution (2-3 weeks).





14•HBF$_4$

Figure S6. Crystal structure of the ion pair of **14**•HBF$_4$ pictured in the manuscript.

Crystal growth method. The salt (150 mg) was dissolved in hot EtOAc (5 mL) and cooled to room temperature. After standing for 3 days, the vial cap was loosened to allow hexanes to diffuse in. After 1 day, crystals had grown and were submitted for analysis.

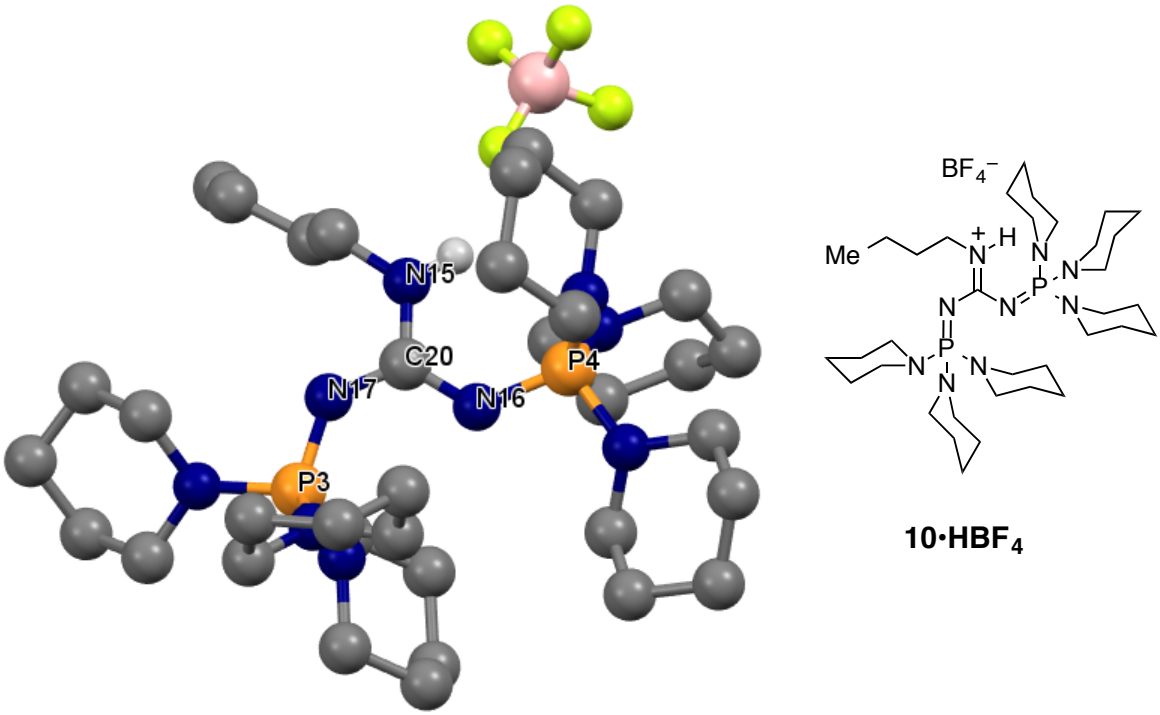


Figure S7. Crystal structure of the ion pair of **10**•HBF_4 pictured in the manuscript.

This structure contains two distinct ion pairs, pictured below. The image above, also shown in the manuscript, is from viewing the structure on the right head on and rotating 120° clockwise.

Note that the quality of this data is lower, with an R-factor of 12.85%. This error likely results from the crystal cracking on cooling under a stream of liquid nitrogen.

Both phosphazene substituents are tilted from the plane of the central guanidinium system:

left substituent:	5.6° below (N16-C20-N17-P3 dihedral angle),	4.1° (other structure)
right substituent:	11.4° above (N15-C20-N16-P4 dihedral angle),	13.1° (other structure)

These substituents also deviate slightly from ideal 120° bond angles to the guanidinium system:

left substituent:	131.6° (C20-N17-P3 angle),	127.7° (other structure)
right substituent:	126.5° (C20-N16-P4 angle) ,	125.0° (other structure)

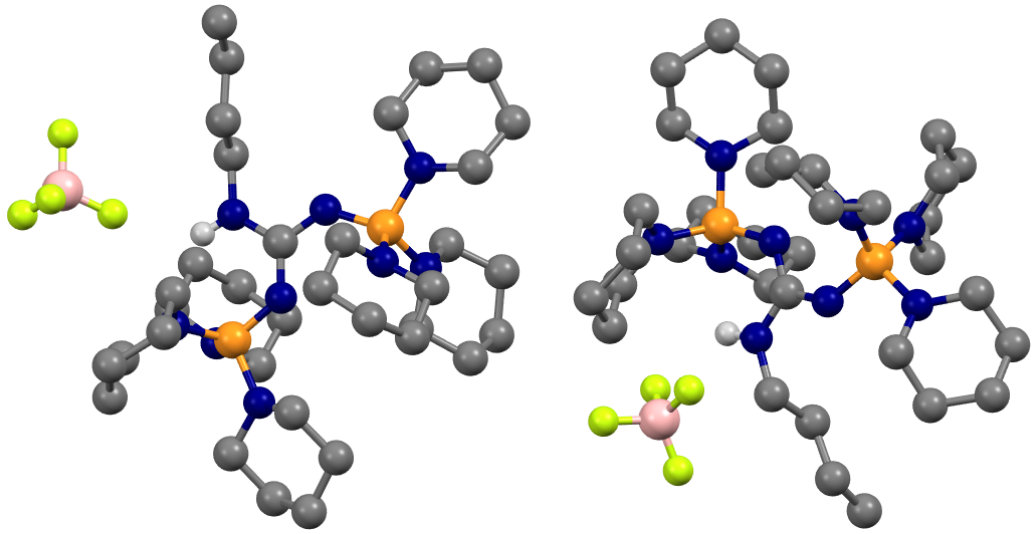


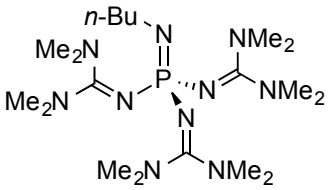
Figure S8. Crystal structure of both ion pairs of **10**•HBF_4.

Crystal growth method. The salt (100 mg) was dissolved in hot EtOAc (5 mL) and cooled to room temperature. After 4 hours, 2 small colorless crystals had already formed so further EtOAc (2 mL) was added to slow their growth. After 2 days, the crystals had each grown to at least 5 mm x 5 mm x 5 mm and were submitted for analysis.

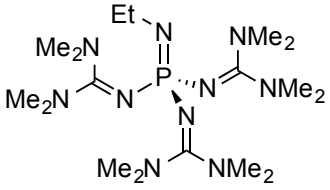
pK_{BH+} Measurements

Notes on PG_3 base 19, P_4 base 21, and PC_3 base 12

As noted in Table 1 of the manuscript, 3 pK_{BH+} values we assigned were not experimentally determined by us.

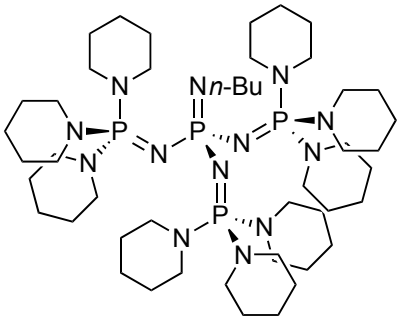


19 synthesized
pK_{BH+} not measured

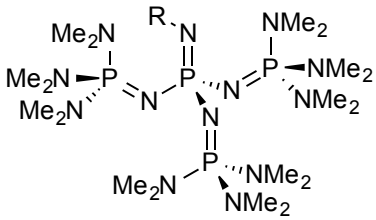


known (ref. 10)
pK_{BH+} = 37.9 (MeCN)

We successfully synthesized the *n*-Bu-PG_3 base **19**, but failed to measure its pK_{BH+} reliably due to the large differences in its value from those of all commercially available standards. Therefore, we extrapolated the reported pK_α value of 29.7 in THF for the *N*-ethyl analogue[10] to a pK_{BH+} value of 37.9 in MeCN as explained at the end of the "*Correction for measurements in d_8-THF and extrapolation to MeCN"* section of this document, and used this result for the PG_3 class.



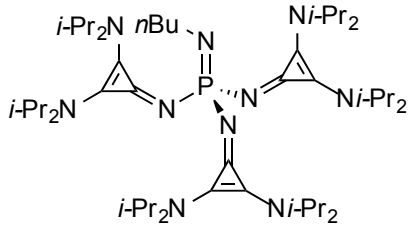
21 not synthesized



known (ref. 7)
pK_{BH+} = 42.7 (MeCN)
R = *t*-Bu, CMe_2CH_2*t*-Bu, CEt_3, CMe_2*t*-Bu

We also experienced difficulties preparing the P_4 base **21** that would contain the *n*-butyl head groups and piperidinyl phosphazene substituents we aimed to use in this study, so we instead assigned the P_4 class in Table 1 a pK_{BH+} of 42.7 in MeCN,[8] the value assigned to all the bulky P_4 bases with dimethylamino tail groups as depicted above. A related phosphazene from this reference containing pyrrolidinyl substituents instead of dimethylamino groups was at least 1.3 pK_{BH+} units more basic, but as the piperidinyl group is usually less π-donating than the pyrrolidinyl group, the dimethylamino series was chosen as the best analogy.

Since we were confident in the aforementioned references and the structural similarities of the compounds discussed in this study to these precedents, we used these results in our data set to help generate the linear regressions shown in Figure 3 of the manuscript.



12

pK_{BH+} = 42.1 estimated from Figure 3

Finally, we were unable fully to purify the PC_3 base **12**, and thus could not measure its pK_{BH+} either. However, since the other 3 members of the phosphazene group in our data set produced an extremely precise linear fit ($R^2 > 0.999$) as shown in Figure 3, we estimated the pK_{BH+} of **12** as 42.1 from this equation and the pK_{BH+} of the substituent (27.6, as determined using C_1 base **17**). We displayed this estimate in Table 1, but it was not used as a data point in Figure 3.

General methodology

Most measurements were conducted in CD_3CN. Solutions were prepared under an argon atmosphere to the extent allowed by a standard dual manifold. The exceptions were the GP_2 and GC_2 bases (**10** and **6**), which were studied in d_8-THF, and for which all solutions were prepared in a glove box.

pK_{BH+} values were measured by mixing stock solutions of the conjugate acid salts of all superbases synthesized herein (0.0667 M, 0.60 mL, 0.040 mmol) and the indicated standard as the free base (0.200 M, 0.20 mL, 0.040 mmol) in sealed NMR tubes. 3 such mixtures were prepared for each compound studied. The resulting solutions were then analyzed by ^{1}H NMR spectroscopy, as well as ^{13}C NMR for the GP_2 and GC_2 compounds. Spectra were acquired between 30 minutes and 2 hours after preparing the solutions. Equilibrium was invariably reached during this interval, and the results were stable after another 12-24 hours.

The signals attributable to both the superbase being studied – the "substrate" – and the standard were then compared to their positions in the spectra of the respective free bases and conjugate acids. Only signals that were sufficiently resolved and that could reliably be assigned a chemical shift (i.e. had symmetric lineshapes) were used. Each such signal then gives an estimate of the ratio of the extent of protonation (or deprotonation) of its corresponding compound, given by

$$\frac{[\mathrm{B}]}{[\mathrm{B}]+[\mathrm{B}\cdot\mathrm{HA}]} = \frac{[\mathrm{B}]}{[\mathrm{B}]_{\mathrm{TOT}}} = \frac{\delta_{\mathrm{B\cdot HA}} - \delta_{\mathrm{obs}}}{\delta_{\mathrm{B\cdot HA}} - \delta_{\mathrm{B}}} \tag{1}$$

and

$$\frac{[\mathrm{B}\cdot\mathrm{HA}]}{[\mathrm{B}]+[\mathrm{B}\cdot\mathrm{HA}]} = \frac{[\mathrm{B}\cdot\mathrm{HA}]}{[\mathrm{B}]_{\mathrm{TOT}}} = \frac{\delta_{\mathrm{obs}} - \delta_{\mathrm{B}}}{\delta_{\mathrm{B\cdot HA}} - \delta_{\mathrm{B}}}, \tag{2}$$

where B denotes either free base and B•HA is its conjugate acid. The ratio of these expressions also gives the ratio of deprotonated to protonated forms of the molecule:

$$\frac{[\mathrm{B}]}{[\mathrm{B}\cdot\mathrm{HA}]} = \frac{\delta_{\mathrm{B\cdot HA}} - \delta_{\mathrm{obs}}}{\delta_{\mathrm{obs}} - \delta_{\mathrm{B}}} \,.^{16} \tag{3}$$

The desired quantity to evaluate is the equilibrium constant for the acid-base reaction

$$\text{substrate} \bullet \mathrm{HA} \;+\; \text{standard} \;\underset{\longleftarrow}{\overset{K_{\mathrm{eq}}}{\longrightarrow}}\; \text{substrate} \;+\; \text{standard} \bullet \mathrm{HA}\,, \tag{4}$$

which is described by the expression

$$K_{\mathrm{eq}} = \frac{[\mathrm{sub}][\mathrm{std}\cdot\mathrm{HA}]}{[\mathrm{sub}\cdot\mathrm{HA}][\mathrm{std}]} \,.^{17} \tag{5}$$

Clearly, the K_{eq} could now be evaluated from using equation (3) for both the substrate and the standard. However, we preferred to generate an estimate of K_{eq} from each individual chemical shift of each component. This procedure allowed us to check the internal consistency of the data – whether the K_{eq} estimates from the chemical shifts of the substrate matched those from the standard – and to estimate uncertainty more easily. As shown below, the estimate of K_{eq} from a single chemical shift value also depends on the ratio of the substrate to the standard, which is most accurately measured by integration of the ^{1}H NMR spectrum (since some stock solutions were prepared volumetrically, there was a modest deviation from 1 to 1 stoichiometry, often 5-10%).

With respect to the substrate, we know from equation (3) that

$$\frac{[\mathrm{sub}]}{[\mathrm{sub}\cdot\mathrm{HA}]} = \frac{\delta_{\mathrm{sub\cdot HA}} - \delta_{\mathrm{obs}}}{\delta_{\mathrm{obs}} - \delta_{\mathrm{sub}}}, \tag{6}$$

but we also need an estimate for

$$\frac{[\mathrm{std}\cdot\mathrm{HA}]}{[\mathrm{std}]} \tag{7}$$

based on the chemical shifts of the substrate. Assuming the only species in solution are the protonated and deprotonated forms of the two components, we know from the stoichiometry that

$$[\mathrm{std}\cdot\mathrm{HA}] = [\mathrm{sub}] \tag{8}$$

16. Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2002**, *67*, 1873.

[17] Similarly to the convention for a generic base B, "sub" and "std" are free bases of the substrate and standard in the system, while "sub•HA" and "std•HA" are their conjugate acids.

since both concentrations are initially zero and these species are produced in a 1 to 1 ratio, and then that

$$[\mathrm{std}] = ([\mathrm{std}] + [\mathrm{std} \cdot \mathrm{HA}]) - [\mathrm{std} \cdot \mathrm{HA}] = [\mathrm{std}]_{\mathrm{TOT}} - [\mathrm{sub}] \tag{9}$$

from the definition of $[\mathrm{std}]_{\mathrm{TOT}}$ and from equation (8). If we next introduce the ratio of total substrate molecules to total standard molecules,

$$r = \frac{[\mathrm{sub}]_{\mathrm{TOT}}}{[\mathrm{std}]_{\mathrm{TOT}}} \tag{10}$$

which can be measured from the ^{1}H NMR spectrum by integration, we can rewrite equation (9) as

$$[\mathrm{std}] = \frac{[\mathrm{sub}]_{\mathrm{TOT}}}{r} - [\mathrm{sub}]\,. \tag{11}$$

Substituting equations (8) and (11) into expression (7) gives

$$\frac{[\mathrm{std} \cdot \mathrm{HA}]}{[\mathrm{std}]} = \frac{[\mathrm{sub}]}{\frac{[\mathrm{sub}]_{\mathrm{TOT}}}{r} - [\mathrm{sub}]} = \frac{1}{\left(\frac{[\mathrm{sub}]_{\mathrm{TOT}} - r[\mathrm{sub}]}{r[\mathrm{sub}]}\right)} = \frac{1}{\frac{1}{r}\left(\frac{[\mathrm{sub}]_{\mathrm{TOT}}}{[\mathrm{sub}]}\right) - 1}, \tag{12}$$

and substituting equation (12) into equation (5) gives

$$K_{\mathrm{eq}} = \frac{\left(\frac{[\mathrm{sub}]}{[\mathrm{sub} \cdot \mathrm{HA}]}\right)}{\frac{1}{r}\left(\frac{[\mathrm{sub}]_{\mathrm{TOT}}}{[\mathrm{sub}]}\right) - 1}. \tag{13}$$

Rewriting equation (13) in terms of chemical shifts, taken from equations (1) and (3) (or (6)), gives

$$K_{\mathrm{eq}} = \frac{\left(\frac{\delta_{\mathrm{sub \cdot HA}} - \delta_{\mathrm{obs}}}{\delta_{\mathrm{obs}} - \delta_{\mathrm{sub}}}\right)}{\frac{1}{r}\left(\frac{\delta_{\mathrm{sub \cdot HA}} - \delta_{\mathrm{sub}}}{\delta_{\mathrm{sub \cdot HA}} - \delta_{\mathrm{obs}}}\right) - 1}. \tag{14}$$

This expression is an estimate of K_{eq} in terms of each chemical shift value of the substrate in the mixture (compared with data from its free base and the conjugate acid) and the ratio of components in the mixture determined by integration. The analogous expression in terms of the standard is

$$K_{\mathrm{eq}} = \frac{\left(\frac{\delta_{\mathrm{obs}} - \delta_{\mathrm{std}}}{\delta_{\mathrm{std\cdot HA}} - \delta_{\mathrm{obs}}}\right)}{r\left(\frac{\delta_{\mathrm{std\cdot HA}} - \delta_{\mathrm{std}}}{\delta_{\mathrm{obs}} - \delta_{\mathrm{std}}}\right) - 1}. \quad (15)$$

Finally, as the basicity of the substrate is described by a reaction of the type

$$\text{substrate} \bullet \text{HA} \xrightleftharpoons{K_{\mathrm{BH+,sub}}} \text{substrate} + \text{HA}, \quad (16)$$

which is the sum of equation (4) and

$$\text{standard} \bullet \text{HA} \xrightleftharpoons{K_{\mathrm{BH+,std}}} \text{standard} + \text{HA}, \quad (17)$$

it follows that each estimate of K_{eq} gives an estimate for the $\mathrm{pK_{BH+}}$ of the substrate described by

$$\mathrm{pK_{BH^+,sub}} = \mathrm{pK_{BH^+,std}} + \mathrm{pK_{eq}} = \mathrm{pK_{BH^+,std}} - \log(K_{\mathrm{eq}}). \quad (18)$$

Obtaining conjugate acids of standards

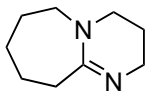
From the preceding discussion, it is clearly necessary to have reference spectra of both the conjugate acids and free bases of both substrates and standards to reliably estimate the substrate's $\mathrm{pK_{BH+}}$.

Standards employed for this analysis (DBU, P_1-*t*Bu(pyrr), and P_2-Et) were obtained commercially as the free bases, so this half of the data was trivial to obtain.

To prepare their conjugate acid salts, the following general procedure was used:

An aqueous solution of HCl (1 M, 1.4 equiv) was added to a solution of the free base (1.0 equiv) in methanol (3 M) at 0 °C. After stirring for 10 minutes, an aqueous solution of $NaBF_4$ (2 M, 1.2 equiv) was added. This solution was then extracted with CH_2Cl_2 (1 volume per volume of water, 2x) and the combined extracts were washed with sat. $NaHCO_3$ (0.5 volumes per volume of CH_2Cl_2) and 2 M $NaBF_4$ (1.0 equiv), dried over Na_2SO_4, and concentrated.

NMR data for free bases and conjugate acids of standards in CD_3CN or *d*$_8$-THF



DBU

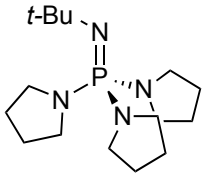
Low yield of the HBF_4 salt (not determined) due to poor partitioning between water and CH_2Cl_2.

HBF_4 salt:[18] ^{1}H NMR (500 MHz, CD_3CN) δ 7.54 (s, 1H), 3.52 (m, 2H), 3.46 (t, *J* = 6.0 Hz, 2H),

18. van der Eide, E. F.; Helm, M. L.; Walter, E. D.; Bullock, R. M. *Inorg*. *Chem*. **2013**, *52*, 1591.

3.28 (t, J = 5.7 Hz, 2H), 2.58 (m, 2H), 1.97 (quint, J = 5.9 Hz, 2H), 1.70 (m, 6H).

Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 3.17 (m, 4H), 3.12 (m, 2H), 2.28 (m, 2H), 1.70 (m, 2H), 1.65 – 1.51 (m, 6H).

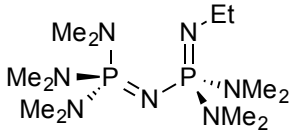


P_1-*t*Bu(pyrr)

The HBF_4 salt was purified by recrystallization from ~ 6:1 EtOAc/hexanes (20 mL) to afford the compound as white needles (1.58 g, 78%).

HBF_4 salt:[5] ^{1}H NMR (500 MHz, CD_3CN) δ 3.63 (d, J = 10.0 Hz, 1H), 3.20 (m, 12H), 1.90 (m, 12H), 1.30 (d, J = 0.8 Hz, 9H).

Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 3.08 (m, 12H), 1.74 (m, 12H), 1.15 (d, J = 1.1 Hz, 9H).



P_2-Et

The HBF_4 salt was purified by mixing 0.5 mmol in *t*-BuOAc (1 mL), cooling to -78 °C for 10 minutes, filtering and washing with hexanes. From this isolation procedure, the yield was significantly lowered (not determined).

HBF_4 salt:[8] ^{1}H NMR (500 MHz, CD_3CN) δ 3.32 (s, 1H), 2.87 (dp, J = 9.7, 7.1 Hz, 2H), 2.65 (m, 30H), 1.12 (td, J = 7.2, 0.8 Hz, 3H).

^{1}H NMR (500 MHz, d_8-THF) δ 4.33 (m, 1H), 2.90 (dp, J = 10.1, 7.0 Hz, 2H), 2.69 (d, J = 10.3 Hz, 30H), 1.15 (td, J = 7.2, 0.9 Hz, 3H).

^{13}C NMR (126 MHz, d_8-THF) δ 37.2, 37.1, 36.7, 17.05 (d, J_{PC} = 7.5 Hz).

Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 2.95 (dq, J = 17.6, 7.1 Hz, 2H), 2.63 (d, J = 10.1 Hz, 19H), 2.56 (d, J = 9.8 Hz, 13H), 0.98 (td, J = 7.1, 1.6 Hz, 3H).

^{1}H NMR (500 MHz, d_8-THF) δ 3.01 (dq, J = 16.7, 7.0 Hz, 2H), 2.66 (d, J = 10.1 Hz, 18H), 2.60 (d, J = 9.6 Hz, 12H), 0.99 (td, J = 7.1, 2.0 Hz, 3H).

^{13}C NMR (126 MHz, d_8-THF) δ 39.9, 38.5, 37.5 (d, J_{PC} = 4.1 Hz), 22.3 (d, J_{PC} = 23.1 Hz).

Obtaining reference spectra of free bases of newly synthesized superbases

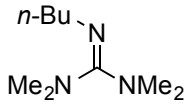
In contrast to standards, new superbases were initially synthesized as their conjugate acid salts.

To obtain reference spectra of fully deprotonated free bases in CD_3CN, the conjugate acid salt (0.050 mmol, 1.0 equiv) was stirred with KO*t*-Bu (28 mg, 0.25 mmol, 5.0 equiv) in CD_3CN (1 mL) for 30 minutes and quickly filtered into an NMR tube. The exception was the PC_1 base, which precipitated from solution on deprotonation, so the isolated free base from the liberation procedure was suspended in CD_3CN in a glove box, sealed in an NMR tube, and heated until it dissolved before obtaining the spectrum.

For the GP_2 and GC_2 bases, a d_8-THF stock solution of the conjugate acid salt (0.0667 M, 0.60 mL, 0.040 mmol) was mixed with a d_8-THF stock solution of P_4-*t*Bu phosphazene base (0.20 M, 0.25-0.35 mL, 0.050-0.070 mmol, 1.25-1.75 equiv)[19] in a glove box.

NMR data for free bases and conjugate acids of new superbases in CD_3CN or d_8-THF

Only signals attributable to the title compounds are listed.

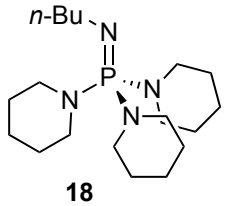


16

HPF_6 salt: ^{1}H NMR (500 MHz, CD_3CN) δ 5.76 (s, 1H), 3.15 (m, 2H), 2.90 (s, 12H), 1.56 (m, 2H), 1.35 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H).

Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 3.07 (t, J = 6.7 Hz, 1H), 2.69 (s, 3H), 2.56 (s, 3H), 1.41 (m, 1H), 1.33 (m, 1H), 0.88 (t, J = 7.3 Hz, 1H).

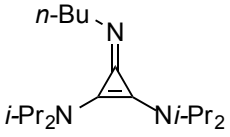
[19] Solid P_4-*t*Bu phosphazene base to prepare the solution was obtained by concentrating a commercial 0.8 M hexane solution under high vacuum in the glove box.



18

HBF_4 salt: ^{1}H NMR (500 MHz, CD_3CN) δ 3.76 (m, 1H), 3.07 (q, J = 6.5 Hz, 12H), 2.90 (dq, J = 8.7, 7.0 Hz, 2H), 1.67 – 1.47 (m, 20H), 1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H).

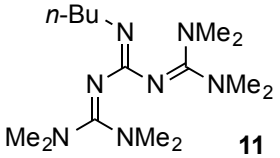
Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 3.02 – 2.91 (m, 14H), 1.54 (m, 6H), 1.45 (quint, J = 5.6 Hz, 12H), 1.33 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H).



17

HBF_4 salt: ^{1}H NMR (500 MHz, CD_3CN) δ 5.74 (s, 1H), 3.84 (hept, J = 6.8 Hz, 4H), 3.37 (q, J = 7.1 Hz, 2H), 1.58 (m, 2H), 1.38 (m, 2H), 1.26 (d, J = 6.9 Hz, 25H), 0.94 (t, J = 7.4 Hz, 3H).

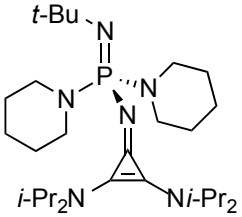
Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 3.67 (hept, J = 6.7 Hz, 4H), 3.25 (t, J = 7.0 Hz, 2H), 1.44 – 1.32 (m, 4H), 1.21 (d, J = 6.8 Hz, 24H), 0.90 (t, J = 7.2 Hz, 3H).



11

HCl salt: ^{1}H NMR (500 MHz, CD_3CN) δ 7.10 (s, 1H), 3.25 (m, 2H), 2.85 (br s, 24H), 1.56 (m, 2H), 1.35 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).

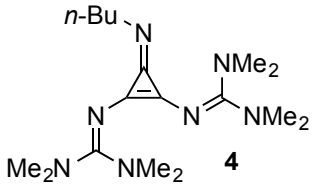
Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 2.98 (t, J = 7.0 Hz, 2H), 2.71 (d, J = 8.4 Hz, 24H), 1.44 (m, 2H), 1.36 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H).



14

HBF_4 salt: ^{1}H NMR (500 MHz, CD_3CN) δ 3.93 (hept, J = 6.8 Hz, 4H), 3.16 (m, 4H), 3.06 (m, 4H), 2.99 (d, J = 11.5 Hz, 1H), 1.63 – 1.49 (m, 12H), 1.29 (d, J = 6.8 Hz, 24H), 1.27 (s, 9H).

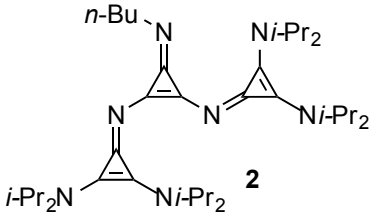
Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 4.07 (br s, 4H), 3.13 (m, 8H), 1.54 – 1.36 (m, 12H), 1.25 (d, J = 6.7 Hz, 24H), 1.09 (br s, 9H).



4

HBF_4 salt: ^{1}H NMR (500 MHz, CD_3CN) δ 6.07 (s, 1H), 3.24 (m, 2H), 2.88 (s, 24H), 1.59 (m, 2H), 1.36 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H).

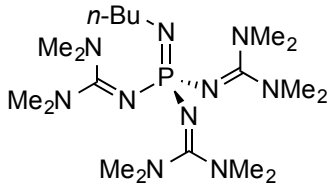
Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 3.05 (t, J = 6.9 Hz, 2H), 2.83 (s, 12H), 2.78 (s, 12H), 1.38 (m, 2H), 1.30 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H).



2

HBF_4 salt: ^{1}H NMR (500 MHz, CD_3CN) δ 5.72 (t, J = 5.7 Hz, 1H), 3.86 (hept, J = 6.8 Hz, 8H), 3.20 (m, 2H), 1.56 (m, 2H), 1.32 (m, 2H), 1.26 (d, J = 6.8 Hz, 48H), 0.90 (t, J = 7.4 Hz, 3H).

Free base: ^{1}H NMR (500 MHz, CD_3CN) δ 3.87 (d, J = 58.2 Hz, 8H), 3.09 (t, J = 6.9 Hz, 2H), 1.36 (m, 2H), 1.31 (m, 2H), 1.24 (d, J = 6.8 Hz, 48H), 0.85 (t, J = 7.3 Hz, 3H).



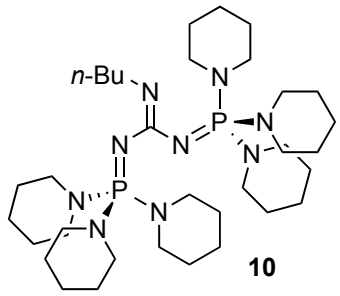
19

HBF_4 salt: ^{1}H NMR (500 MHz, d_8-THF) δ 3.48 (dt, J = 11.4, 6.7 Hz, 1H), 2.88 (s, 36H), 2.77 (m, 2H), 1.48 (m, 2H), 1.31 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, d_8-THF) δ 161.6, 42.0, 40.5, 34.9 (d, J_{PC} = 7.6 Hz), 21.1, 14.3.

Free base: ^{1}H NMR (500 MHz, d_8-THF) δ 3.01 (dt, J = 16.9, 6.1 Hz, 2H), 2.80 (s overlapping with m, 40H), 0.84 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, d_8-THF) δ 158.3, 47.1, 40.4, 40.1, 21.7, 15.0.



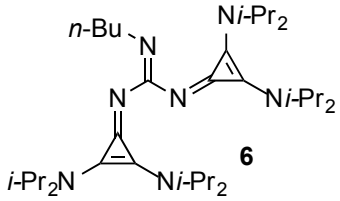
10

HBF_4 salt: ^{1}H NMR (500 MHz, d_8-THF) δ 5.63 (m, 1H), 3.33 (m, 2H), 3.15 (br s, 24H), 1.65 – 1.50 (m, 38H), 1.32 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, d_8-THF) δ 159.2, 47.1, 43.9, 32.9, 27.2 (d, J_{PC} = 5.4 Hz), 21.1, 14.3.

Free base: ^{1}H NMR (500 MHz, d_8-THF) δ 3.12 (m, 26H), 1.56 – 1.42 (m, 36H), 0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, d_8-THF) δ 158.1, 50.7 (d, J_{PC} = 6.0 Hz), 47.4 (d, J_{PC} = 34.1 Hz), 36.2, 27.7 (d, J_{PC} = 5.5 Hz), 27.6 (d, J_{PC} = 5.5 Hz), 26.2 (d, J_{PC} = 5.6 Hz), 22.2, 15.0.



6

HBF_4 salt: ^{1}H NMR (500 MHz, d_8-THF) δ 5.79 (t, J = 5.7 Hz, 1H), 4.00 (br s, 8H), 3.31 (m, 2H), 1.60 (m, 2H), 1.29 (d overlapping with m, J = 6.9 Hz, 48H and 2H), 0.89 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, d_8-THF) δ 162.2, 51.0, 43.4 33.0, 22.2, 21.2, 14.4.

Free base: ^{1}H NMR (500 MHz, d_8-THF) δ 4.20 (quint, J = 6.8 Hz, 4H), 3.82 (quint, J = 6.7 Hz, 4H), 3.25 (t, J = 7.1 Hz, 2H), 1.42 (m, 3H), 1.24 (d, J = 4.9 Hz, 24H), 1.23 (d, J = 4.9 Hz, 24H), 0.86 (t, J = 7.3 Hz, 4H).

^{13}C NMR (126 MHz, d_8-THF) δ 166.6, 124.7, 124.6, 116.0, 115.4, 49.7, 49.4, 35.8, 22.7, 22.6, 22.4, 22.1, 14.9.

Results of pK_{BH+} measurements

Procedure for data analysis

The procedures described above were used to generate the following data. For each mixture of the indicated substrate and standard, each column represents the pK_{BH+} values estimated by the indicated NMR signal. Each row represents one experiment. The final pK_{BH+} is the equally weighted mean of two means: the mean value predicted from all substrate signals and the mean

value predicted from all standard signals, to avoid giving greater weight to the compound with a greater number of usable signals. The uncertainty is estimated by the standard deviation of the entire data set.

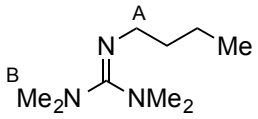
Representative NMR spectra for this section follow the standard spectra that support the synthetic procedures at the end of this document. Data for the conjugate acid and the free base of the standards are shown first, followed by the conjugate acid, the free base, and one representative pK_{BH+} experiment for all of the substrates studied. In the latter spectra, only the data used to obtain the tabulated results is labeled, including the integrations used to determine the ratio of substrate to standard.

Literature values for the standards were as follows: DBU, pK_{BH+} = 24.34 (MeCN);[20] P_1-*t*Bu(pyrr), pK_{BH+} = 28.35 (MeCN),[5] P_2-Et pK_{BH+} = 32.94 (MeCN),[8] P_2-Et pK_{α} = 25.3 (THF).[21]

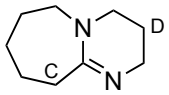
20. Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019.

21. Garrido, G.; Koort, E.; Ràfols, C.; Bosch, E.; Rodima, T.; Leito, I.; Rosés, M. *J. Org. Chem.* **2006**, *71*, 9062.

Measurements in CD_3CN (all based on ^1H NMR spectroscopy)



16

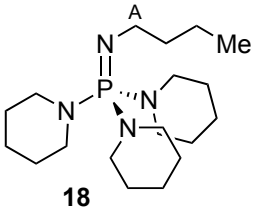


DBU
pK_{BH+} = 24.34

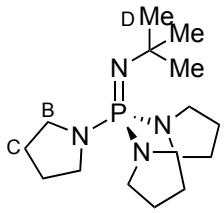
signal	A	B
trial 1	24.6196	24.7719
trial 2	24.6269	24.7779
mean	24.6233	24.7749
std. dev.	0.0051	0.0043

C	D
24.9908	24.9410
24.9934	24.9443
24.9921	24.9427
0.0019	0.0023

Overall for G_1: $\mathbf{pK_{BH^+} = 24.8 \pm 0.2}$



18

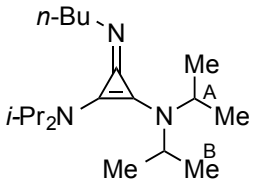


P_1-*t*Bu(pyrr)
pK_{BH+} = 28.35

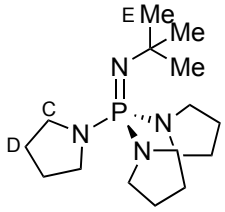
signal	A
trial 1	27.8493
trial 2	27.8670
trial 3	27.8512
mean	27.8558
std. dev.	0.0097

B	C	D
27.7916	27.7922	27.7940
27.7788	27.7811	27.7799
27.7860	27.7881	27.7886
27.7855	27.7871	27.7875
0.0064	0.0056	0.0071

Overall for P_1: $\mathbf{pK_{BH^+} = 27.82 \pm 0.03}$



17

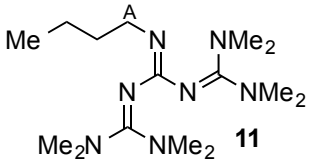


P_1-*t*Bu(pyrr)
pK_{BH+} = 28.35

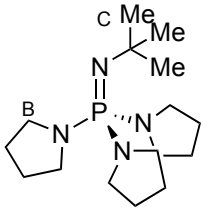
signal	A	B
trial 1	27.5357	27.5978
trial 2	27.5405	27.6019
trial 3	27.5452	27.6112
mean	27.5404	27.6036
std. dev.	0.0047	0.0069

C	D	E
27.5410	27.5508	27.5444
27.5354	27.5447	27.5397
27.5316	27.5384	27.5364
27.5360	27.5446	27.5401
0.0047	0.0062	0.0040

Overall for C_1: $\mathbf{pK_{BH^+} = 27.56 \pm 0.03}$



11

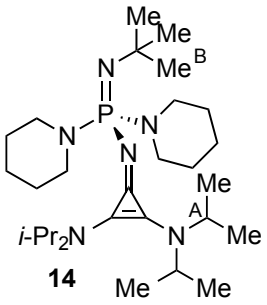


P_1-*t*Bu(pyrr)
pK_{BH+} = 28.35

signal	A
trial 1	29.4737
trial 2	29.4738
trial 3	29.4757
mean	29.4744
std. dev.	0.0011

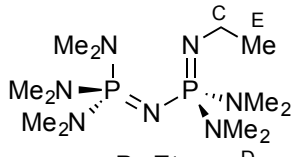
B	C
29.4119	29.5468
29.4168	29.5516
29.4121	29.5486
29.4136	29.5490
0.0027	0.0024

Overall for G_3: $\mathbf{pK_{BH^+} = 29.48 \pm 0.06}$



14

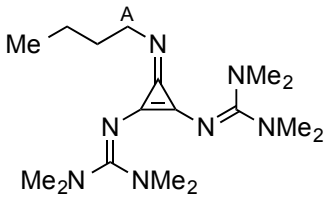
signal	A	B
trial 1	31.7609	31.6827
trial 2	31.7034	31.6597
trial 3	31.7099	31.6136
mean	31.7247	31.6520
std. dev.	0.0315	0.0352



P_2-Et
pK_{BH+} = 32.94

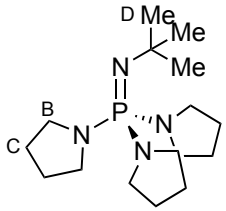
C	D	E
31.6212	31.8937	31.7343
31.6708	31.9249	31.9758
31.6745	31.8899	31.9524
31.6555	31.9028	31.8875
0.0297	0.0192	0.1332

Overall for PC_1: $\mathbf{pK_{BH^+} = 31.8 \pm 0.1}$



4

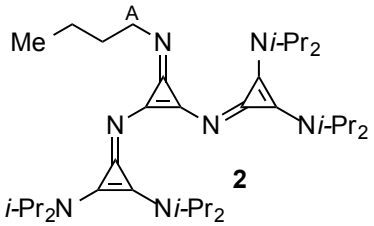
signal	A
trial 1	28.9064
trial 2	28.9009
trial 3	28.9056
mean	28.9043
std. dev.	0.0030



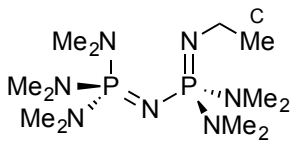
P_1-*t*Bu(pyrr)
pK_{BH+} = 28.35

B	C	D
28.9687	29.0148	28.9872
28.9708	29.0194	28.9881
28.9796	29.0251	28.9969
28.9730	29.0198	28.9907
0.0057	0.0052	0.0053

Overall for CG_2: $\mathbf{pK_{BH^+} = 28.95 \pm 0.04}$



2



P$_2$-Et

pK_{BH+} = 32.94

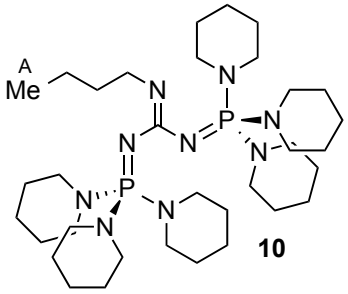
signal	A
trial 1	31.6256
trial 2	31.6305
trial 3	31.6736
mean	31.6432
std. dev.	0.0264

B	C
31.5346	31.5118
31.5191	31.5089
31.5205	31.4767
31.5247	31.4991
0.0086	0.0195

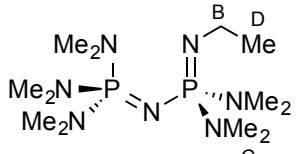
Overall for C_3: $\mathbf{pK_{BH^+} = 31.57 \pm 0.07}$

Measurements in d_8-THF (based on ^{1}H and ^{13}C NMR spectroscopy)

^{1}H NMR data



10

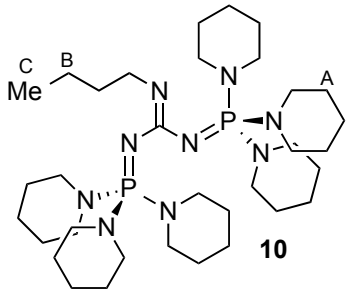


P_2-Et
pK_α = 25.3

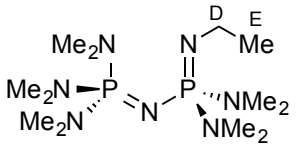
signal	A
trial 1	26.3262
trial 2	26.3141
trial 3	26.3115
mean	26.3173
std. dev.	0.0079

B	C	D
26.3607	26.3374	26.3186
26.3589	26.3416	26.3217
26.3661	26.3483	26.3268
26.3619	26.3424	26.3224
0.0038	0.0055	0.0041

^{13}C NMR data



10



P_2-Et
pK_α = 25.3

signal	A	B	C
trial 1	26.2949	26.3978	26.2432
trial 2	26.2973	26.3124	26.2380
trial 3	26.2849	26.3384	26.2578
mean	26.2924	26.3495	26.2463
std. dev.	0.0066	0.0437	0.0102

D	E
26.3273	26.3433
26.2196	26.2422
26.2736	26.2914
26.2735	26.2923
0.0539	0.0506

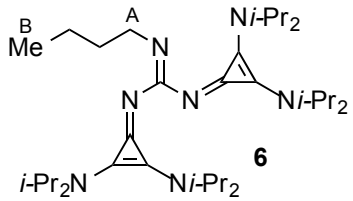
Uncorrected for GP_2:[22] $pK_{ip'} = 26.3096 \pm 0.0438$ (THF)

Corrected for GP_2: $pK_\alpha = 26.5092 \pm 0.0438$ (THF)

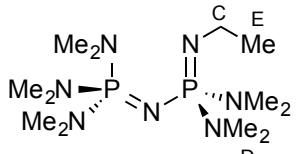
Extrapolation for GP_2: $\mathbf{pK_{BH^+} = 34.34 \pm 0.05}$ **(MeCN)**

[22] This is a convenient placeholder to illustrate our calculation procedure but has no physical meaning, as explained in the following section. That section also explains the correction and extrapolation in detail.

^{1}H NMR data



6

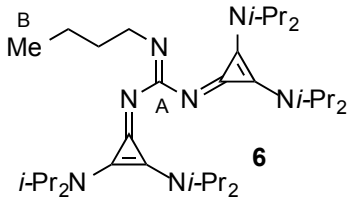


P$_2$-Et
pK$_\alpha$ = 25.3

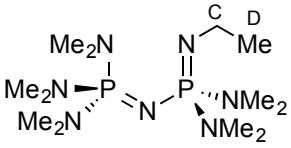
signal	A	B
trial 1	27.2319	27.5636
trial 2	27.2611	27.6037
trial 3	27.3125	27.5954
mean	27.2685	27.5875
std. dev.	0.0408	0.0212

C	D	E
27.5424	27.5170	27.4738
27.5323	27.4817	27.4506
27.4727	27.4045	27.3811
27.5158	27.4678	27.4351
0.0377	0.0576	0.0482

^{13}C NMR data



6



P$_2$-Et
pK$_\alpha$ = 25.3

signal	A	B
trial 1	27.3775	27.3610
trial 2	27.5822	27.3217
trial 3	27.5022	27.2834
mean	27.4873	27.3220
std. dev.	0.1032	0.0388

C	D
27.2945	27.3738
26.7725	26.8336
26.8738	26.9344
26.9803	27.0473
0.2768	0.2872

Uncorrected for GC$_2$:[23] $\mathrm{pK_{ip}}, = 27.3298 \pm 0.2353$ (THF)

Corrected for GC$_2$: $\mathrm{pK_\alpha} = 27.6558 \pm 0.2353$ (THF)

Extrapolation for GC$_2$: $\mathbf{pK_{BH^+} = 35.6 \pm 0.3}$ **(MeCN)**

Correction for measurements in d_8-THF and extrapolation to MeCN

In polar solvents such as acetonitrile, differences in pK_{BH+} values can be estimated directly from the relative concentrations of free base and conjugate acid of each component. However, in low-dielectric solvents such as THF, ion pairing is significant, and factoring this behavior into pK_{BH+} measurements gives a more meaningful estimate of basicity, and better correlations with other

[23] This is a convenient placeholder to illustrate our calculation procedure but has no physical meaning, as explained in the following section. That section also explains the correction and extrapolation in detail.

solvents.[24]

Therefore, relative pK_{BH+} differences determined without such a correction are referred to as ion pair basicities, pK_{ip}. After correcting for the degree of ion pairing, which relates primarily to the size of the ions – larger ions tend to form closer contact pairs – the better estimate of basicity, termed the free ion basicity, pK_{α}, is obtained.

Since the pK_{α} of the P_2-Et phosphazene standard is known, we can estimate the pK_{α} of the GP_2 and GC_2 bases using the ΔpK_{ip}, measured by NMR spectroscopy, and an estimate of the dissociation constants of the ions, K_d:

$$\mathrm{pK}_{\alpha,\mathrm{sub}} - \mathrm{pK}_{\alpha,\mathrm{std}} = \mathrm{pK}_{\mathrm{ip,sub}} - \mathrm{pK}_{\mathrm{ip,std}} - \log\left(\frac{K_{\mathrm{d,std\cdot HA}}}{K_{\mathrm{d,sub\cdot HA}}}\right) \tag{19}$$

Since ΔpK_{ip} and $pK_{\alpha,std}$ are known, the last quantities required to determine $pK_{\alpha,sub}$ are $K_{d,std\bullet HA}$ and $K_{d,sub\bullet HA}$ (note that before correction, the "uncorrected" basicity estimate we have labeled "$pK_{ip'}$" corresponds to $pK_{ip'} = pK_{\alpha,std} + \Delta pK_{ip}$, a physically meaningless quantity). A model for ion pair dissociation constants developed by Fuoss[25] estimates that

$$K_{\mathrm{d}} = \frac{3000e^{b}}{4\pi N a^{3}} \tag{20}$$

where e is the base of natural logarithms, N is the Avogradro constant, a is the inter-ion distance, and

$$b = \frac{-e^{2}}{a\epsilon kT} \tag{21}$$

wherein e is the elementary charge, a is again the inter-ion distance, ϵ is the dielectric constant of the medium, k is the Boltzmann constant, and T is temperature.

With one exception, all of these quantities are either constants,

$$N = 6.02214\times 10^{23}\ \mathrm{mol}^{-1}, \tag{22}$$

$$e = 4.80\times 10^{-10}\mathrm{erg}^{\frac{1}{2}}\cdot\mathrm{cm}^{\frac{1}{2}}, \tag{23}$$

$$k = 1.38065\times 10^{-16}\mathrm{erg}\cdot\mathrm{K}^{-1}, \tag{24}$$

or are known,

---

24. (a) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155. (b) Kaljurand, I.; Rodima, T.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A.; Mishima, M. *J. Org. Chem.* **2003**, *68*, 9988.
25. Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.

$$\epsilon = 7.6 \text{ (for THF)}\,, \tag{25}$$

$$T = 300\ \text{K}\,, \tag{26}$$

so estimating the pK_α of the GP_2 and GC_2 bases only requires an approximation for the inter-ion distances of the GP_2•HBF_4 and GC_2•HBF_4 ion pairs, as well as the P_2-Et•HBF_4 ion pair (the actual distances of interest are sums of the respective cationic radii of GP_2H^+, GC_2H^+, P_2-EtH^+, and the anionic radius of BF_4^-). It has previously been estimated by semi-empirical methods[10] that

$$r_{\mathrm{P_2EtH^+}} = 4.8\ \text{Å}\,, \tag{27}$$

$$r_{\mathrm{BF_4^-}} = 2\ \text{Å}\,. \tag{28}$$

Finally, since we obtained crystal structures of GP_2•HBF_4 and GC_2•HBF_4, we analyzed the data and determined the cationic volumes

$$V_{\mathrm{GP_2H^+}} = 600.385\ \text{Å}^3\,, \tag{29}$$

$$V_{\mathrm{GC_2H^+}} = 714.03\ \text{Å}^3\,, \tag{30}$$

which from the (admittedly crude) approximation of the ions as spheres, estimates that the cationic radii are

$$r_{\mathrm{GP_2H^+}} = 5.233\ \text{Å}\,, \tag{31}$$

$$r_{\mathrm{GC_2H^+}} = 5.545\ \text{Å}\,, \tag{32}$$

and thus the inter-ion distances required are

$$a_{\mathrm{P_2Et\cdot HBF_4}} = 6.8\ \text{Å}\,, \tag{33}$$

$$a_{\mathrm{GP_2\cdot HBF_4}} = 7.233\ \text{Å}\,, \tag{34}$$

$$a_{\mathrm{GC_2\cdot HBF_4}} = 7.545\ \text{Å}\,. \tag{35}$$

Substituting these estimates of *a* as well as the quantities given in equations (21)-(26), we obtain the approximations

$$K_{\mathrm{d,P_2Et\cdot HBF_4}} = 2.667\times10^{-5}\ \text{mol}\cdot\text{cm}^{-3}, \tag{36}$$

$$K_{\mathrm{d,GP_2\cdot HBF_4}} = 4.223\times10^{-5}\ \text{mol}\cdot\text{cm}^{-3}, \tag{37}$$

$$K_{\mathrm{d,GC_2\cdot HBF_4}} = 4.223\times10^{-5}\ \mathrm{mol\cdot cm^{-3}}, \tag{38}$$

which leads to the correction factors

$$-\log\left(\frac{K_{\mathrm{d,P_2Et\cdot HBF_4}}}{K_{\mathrm{d,GP_2\cdot HBF_4}}}\right) = 0.1996\,, \tag{39}$$

$$-\log\left(\frac{K_{\mathrm{d,P_2Et\cdot HBF_4}}}{K_{\mathrm{d,GC_2\cdot HBF_4}}}\right) = 0.3260\,, \tag{40}$$

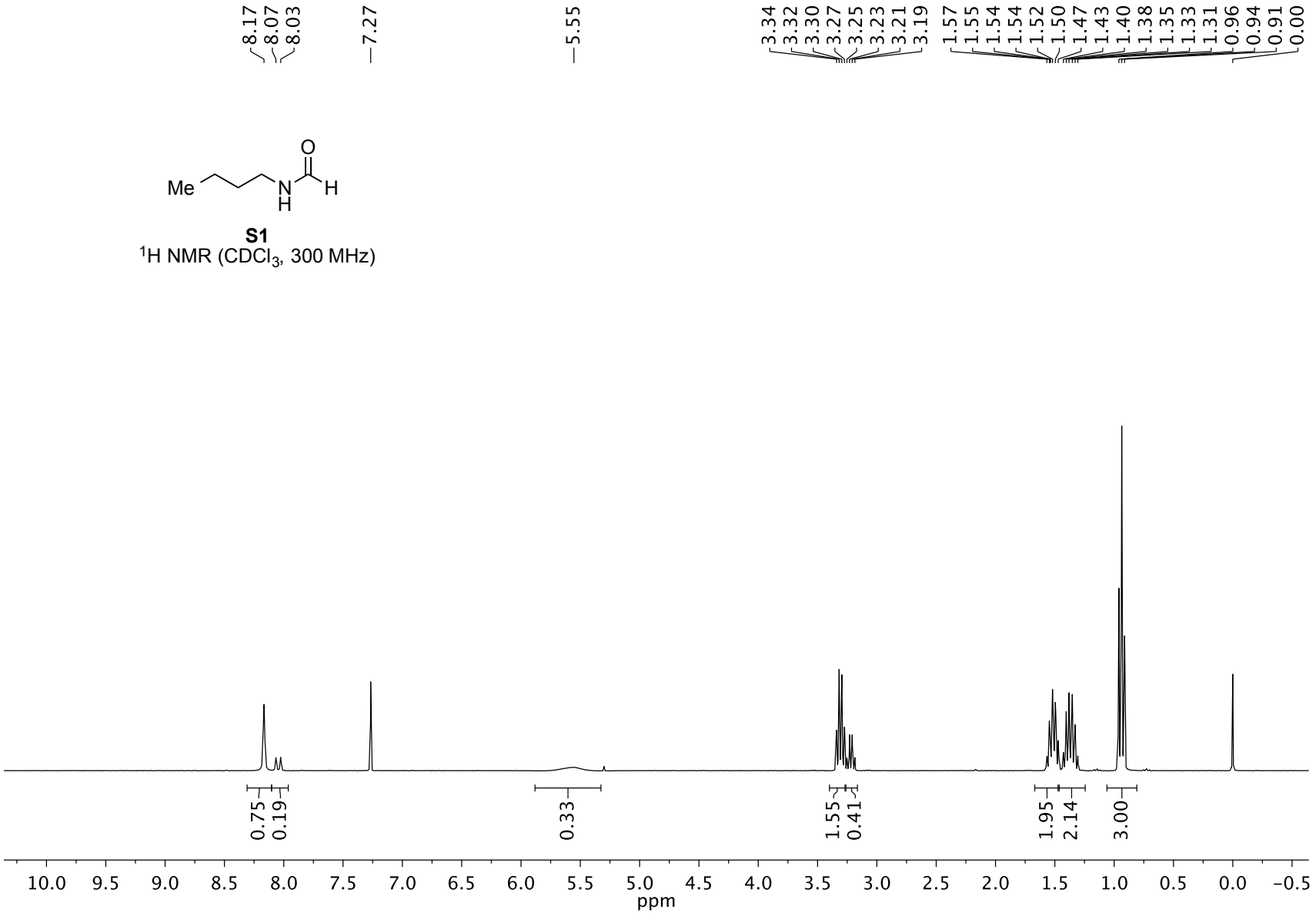
meaning that 0.1996 and 0.3260 must be added respectively to the uncorrected "pK_{ip}" values for GP_2 and GC_2 bases obtained directly from NMR data in order to estimate their pK_α values.

Finally, to extrapolate the pK_α values measured in THF for these bases to acetonitrile, we simply applied the more extensive correlation of 77 bases determined by Leito, Jahn, and coworkers[26] that

$$\mathrm{pK_{\alpha,THF}} = 0.90(2)\mathrm{pK_{BH^+,MeCN}} - 4.4(4). \tag{41}$$

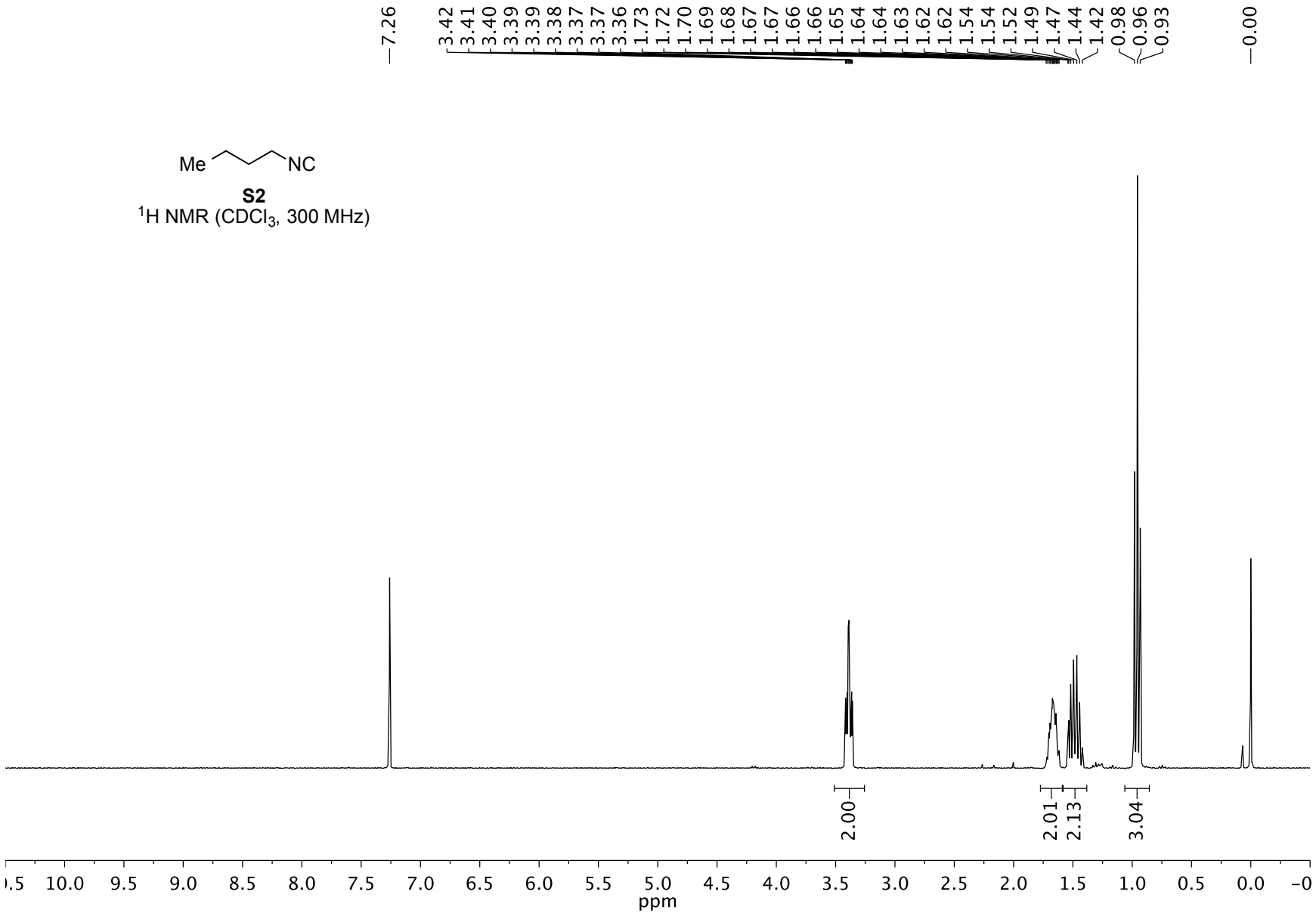
26. Vazdar, K.; Kunetskiy, R.; Saame, J.; Kaupmees, K.; Leito, I.; Jahn, U. *Angew. Chem. Int. Ed.* **2014**, *53*, 1435.

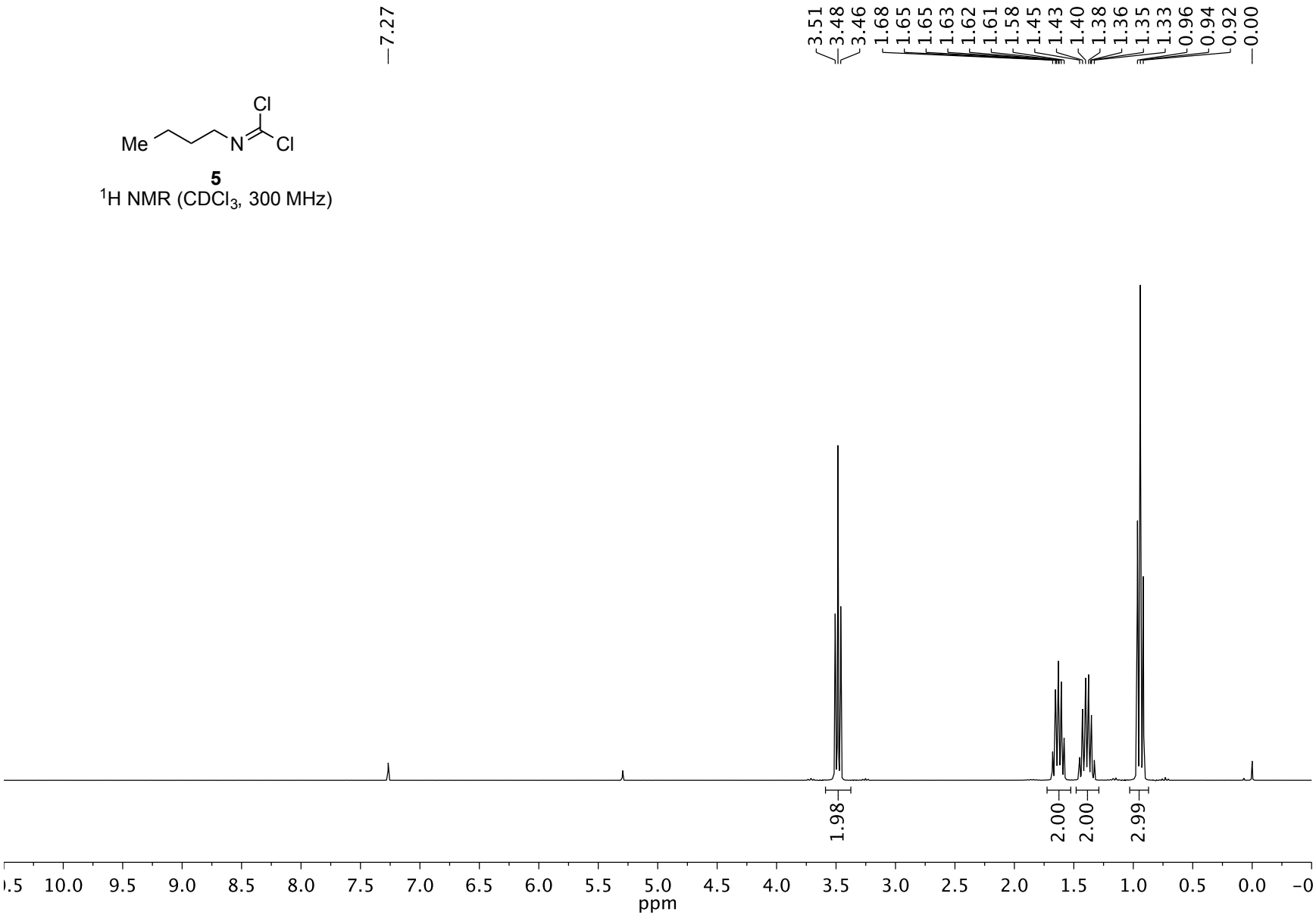
NMR Spectra



S1

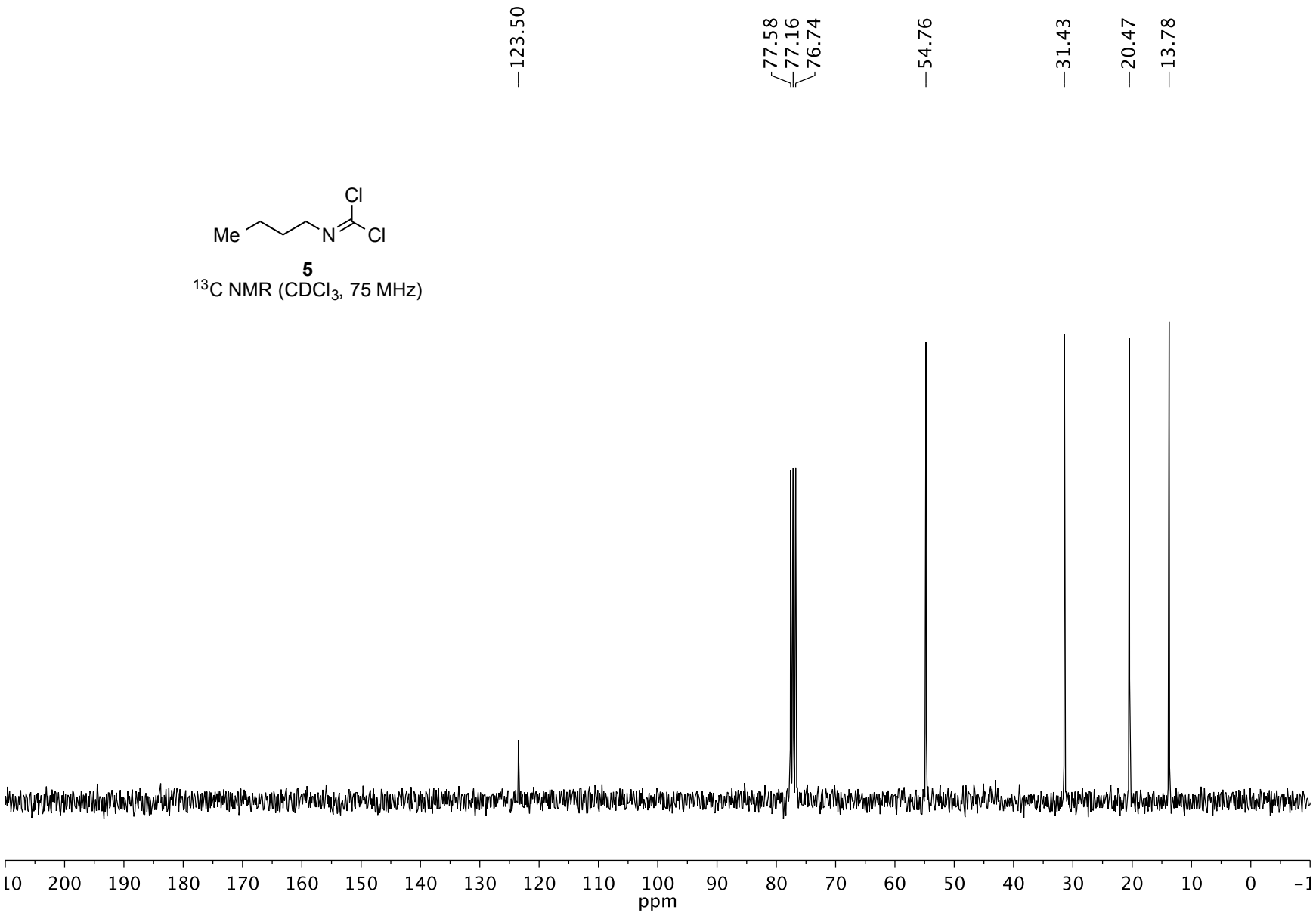
^{1}H NMR ($CDCl_3$, 300 MHz)

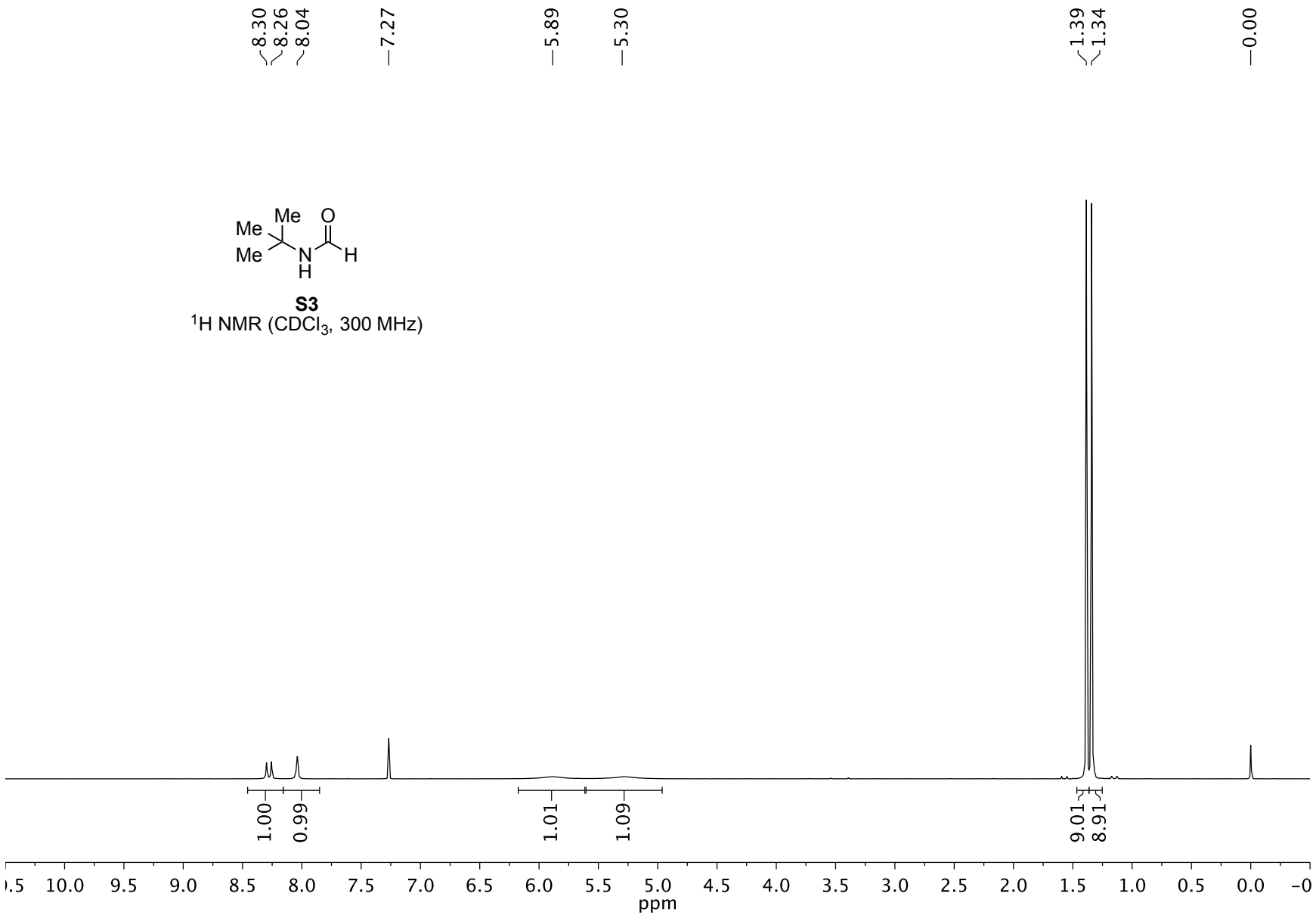

7.26
3.42
3.41
3.40
3.39
3.39
3.38
3.37
3.37
3.36
1.73
1.72
1.70
1.69
1.68
1.67
1.67
1.66
1.66
1.65
1.64
1.64
1.63
1.62
1.62
1.54
1.54
1.52
1.49
1.47
1.44
1.42
0.98
0.96
0.93
0.00
Me
NC
S2
1H NMR (CDCl3, 300 MHz)
2.00
2.01
2.13
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



5

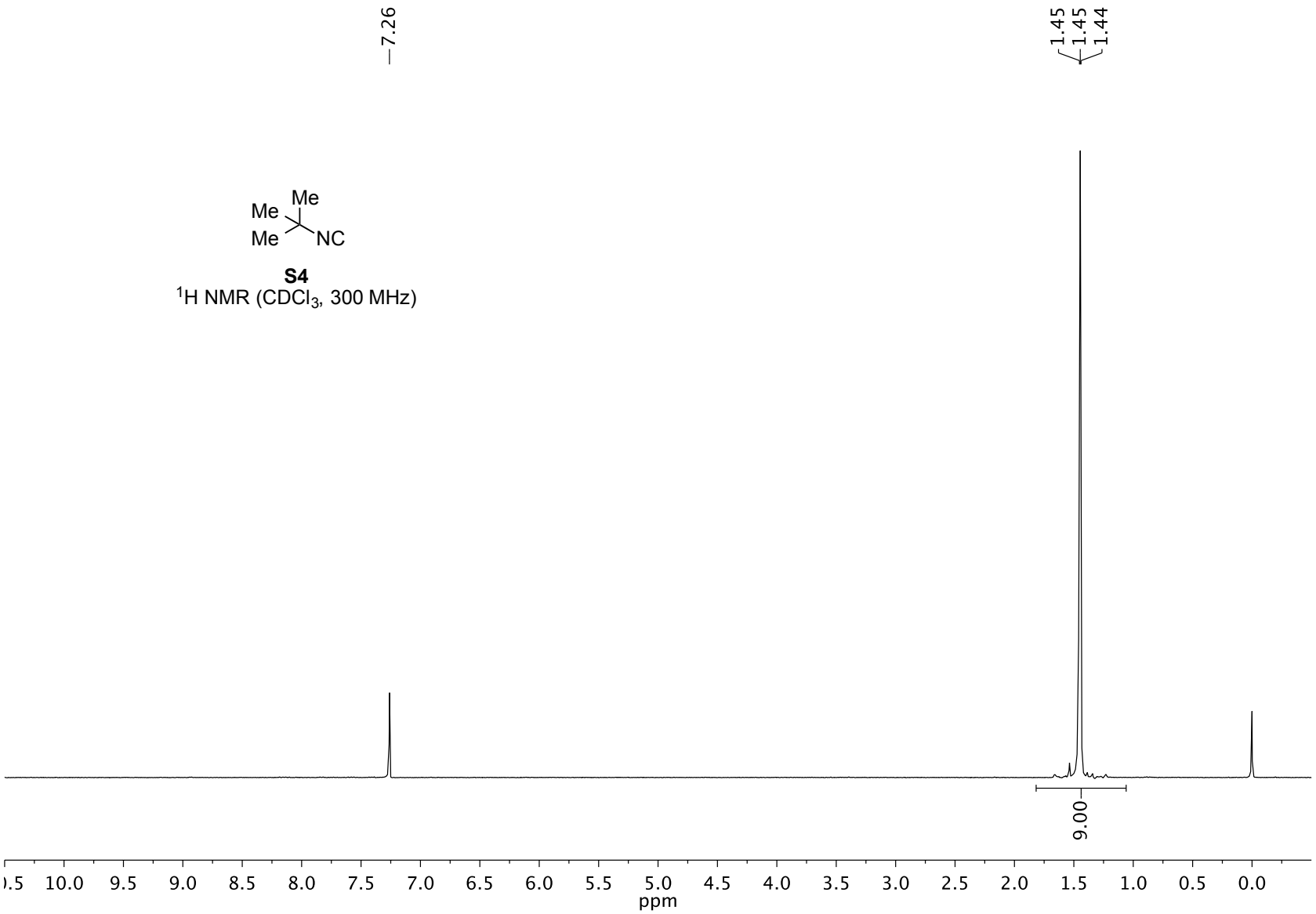
^{1}H NMR ($CDCl_3$, 300 MHz)


123.50
77.58
77.16
76.74
54.76
31.43
20.47
13.78
Me
N
Cl
Cl
5
13C NMR (CDCl3, 75 MHz)
ppm



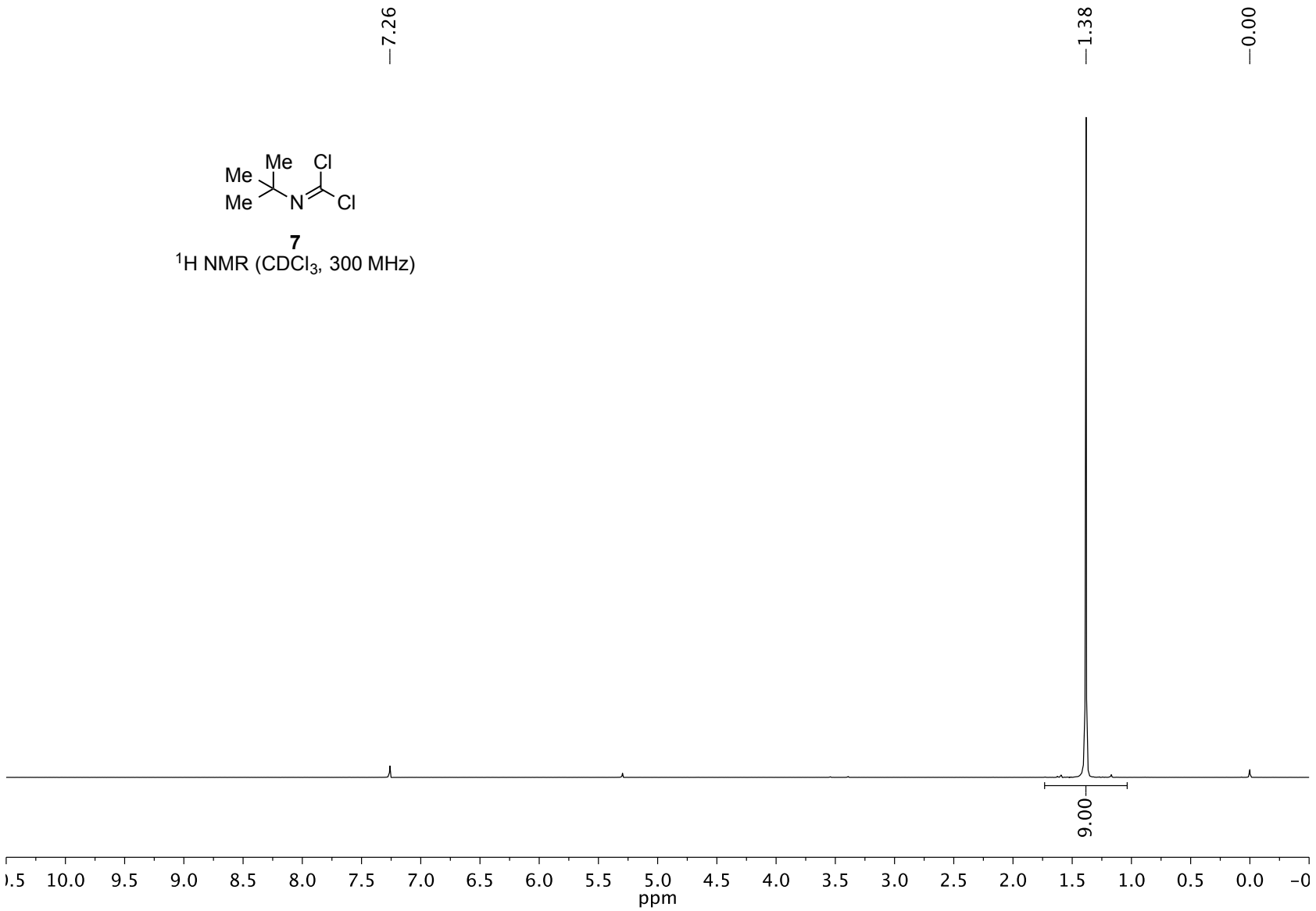
S3

^{1}H NMR ($CDCl_3$, 300 MHz)



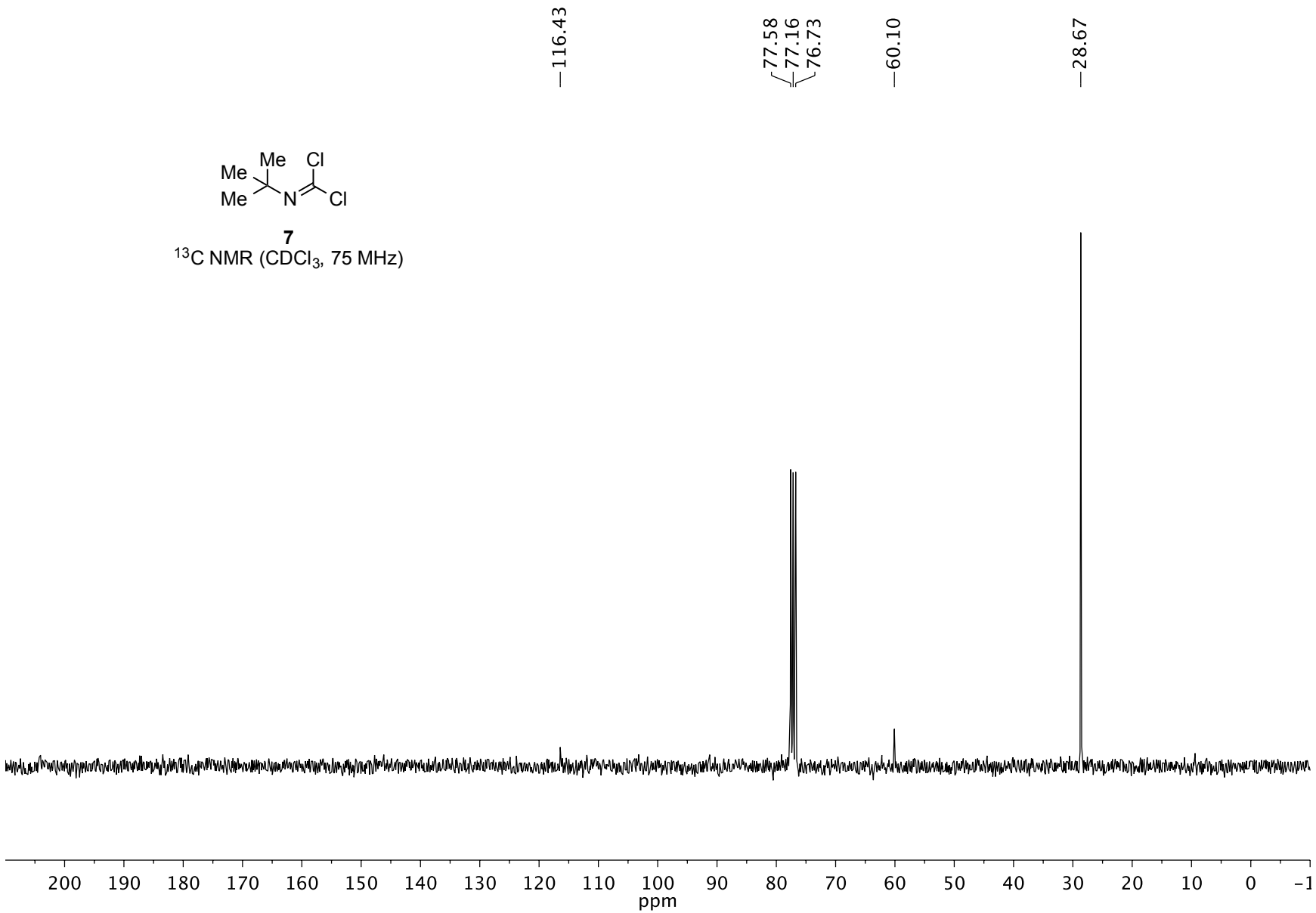
S4

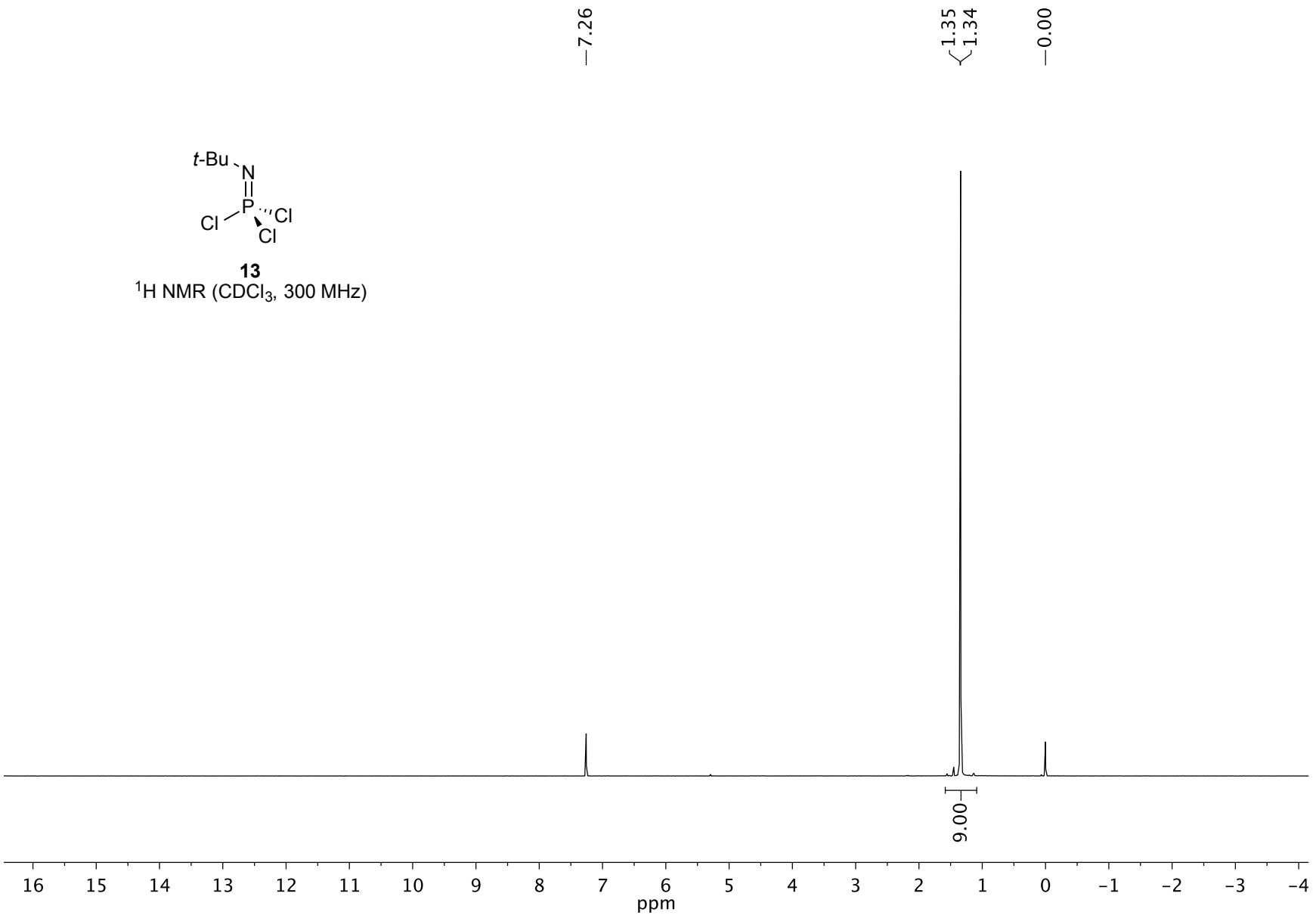
^{1}H NMR ($CDCl_3$, 300 MHz)



7

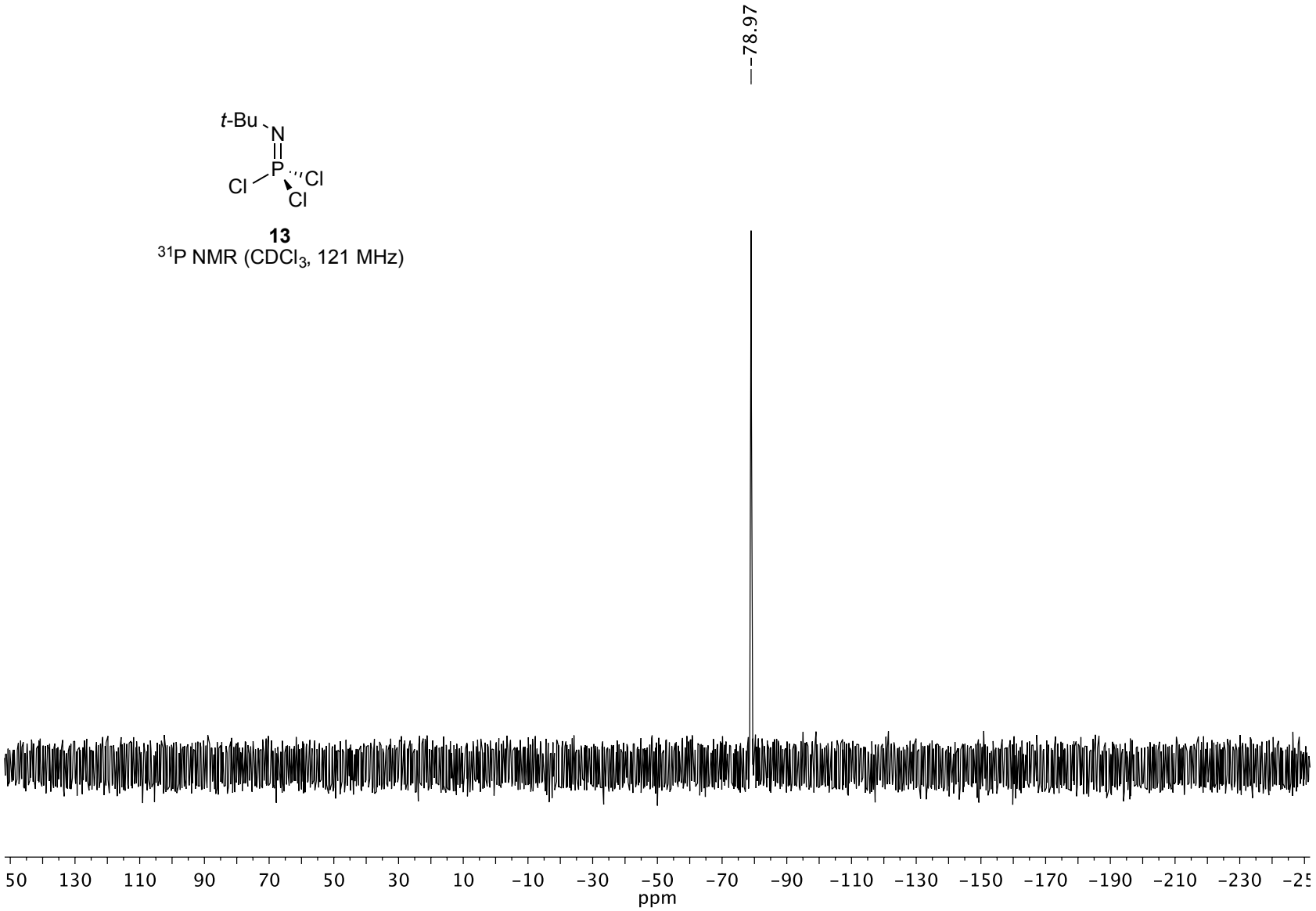
^{1}H NMR ($CDCl_3$, 300 MHz)


116.43
77.58
77.16
76.73
60.10
28.67
Me
Me
Me
Cl
Cl
N
7
13C NMR (CDCl3, 75 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm



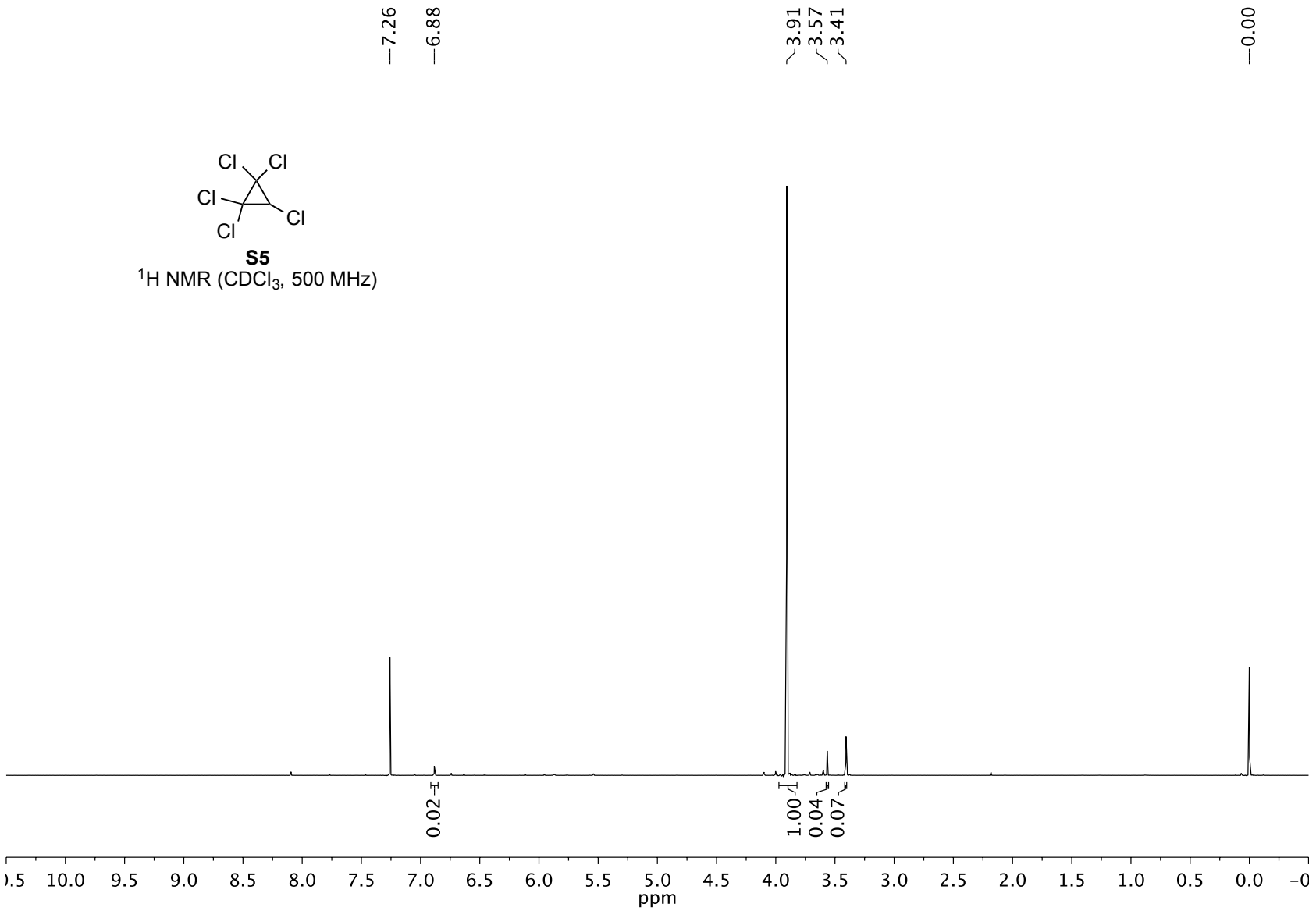
13

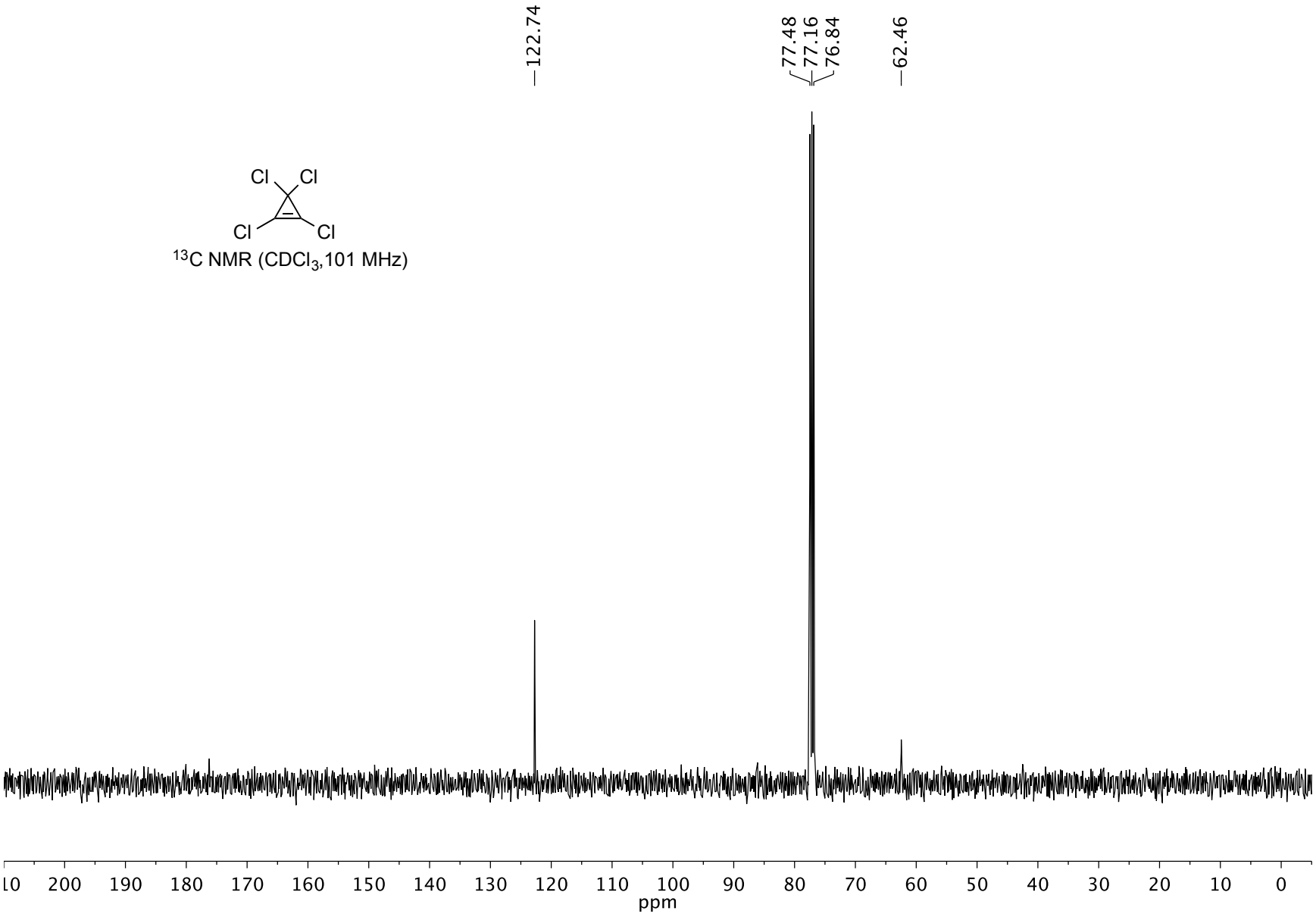
^{1}H NMR ($CDCl_3$, 300 MHz)

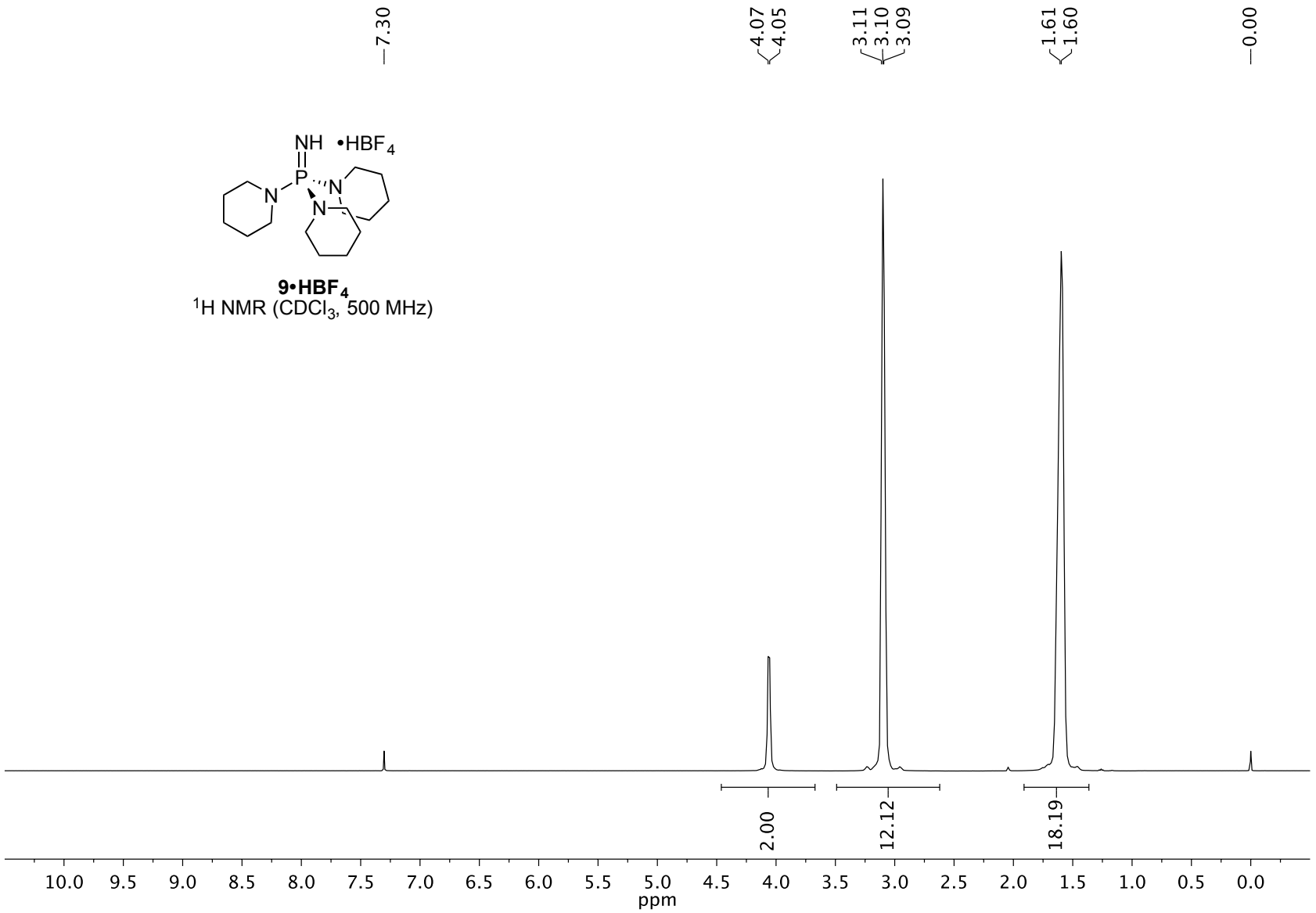


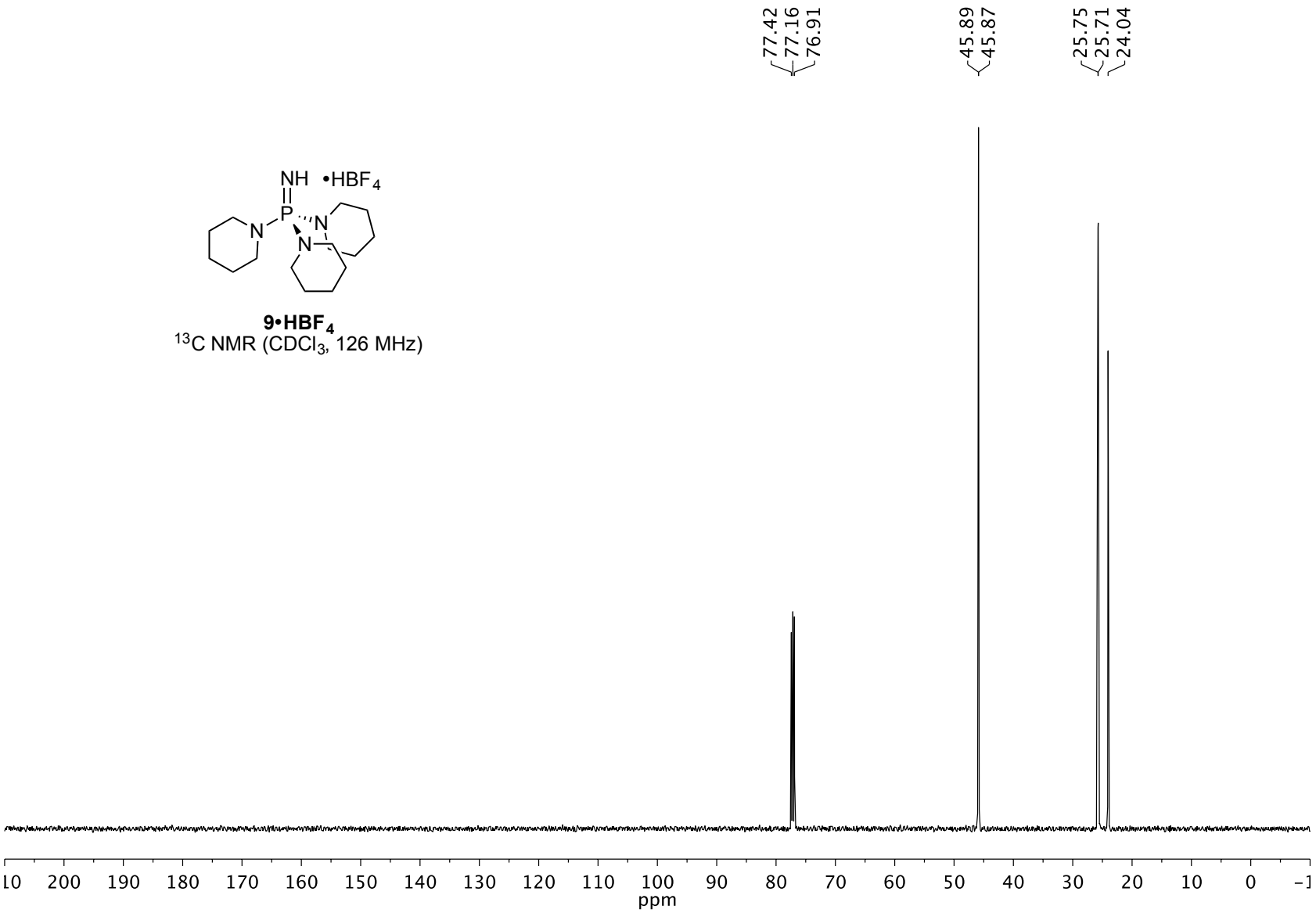
13

^{31}P NMR ($CDCl_3$, 121 MHz)

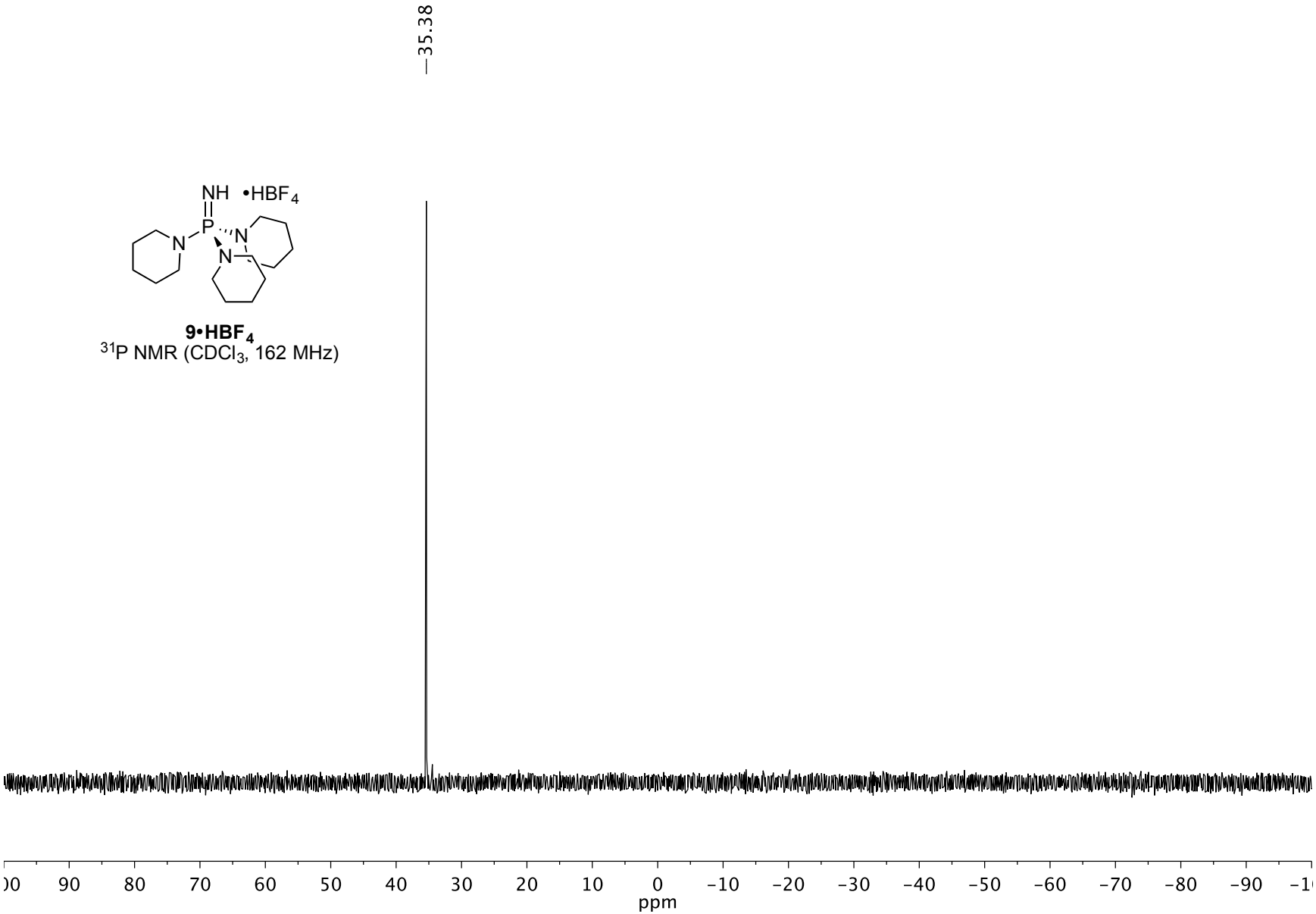

7.26
6.88
3.91
3.57
3.41
0.00
Cl
Cl
Cl
Cl
Cl
S5
1H NMR (CDCl3, 500 MHz)
0.02
1.00
0.04
0.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

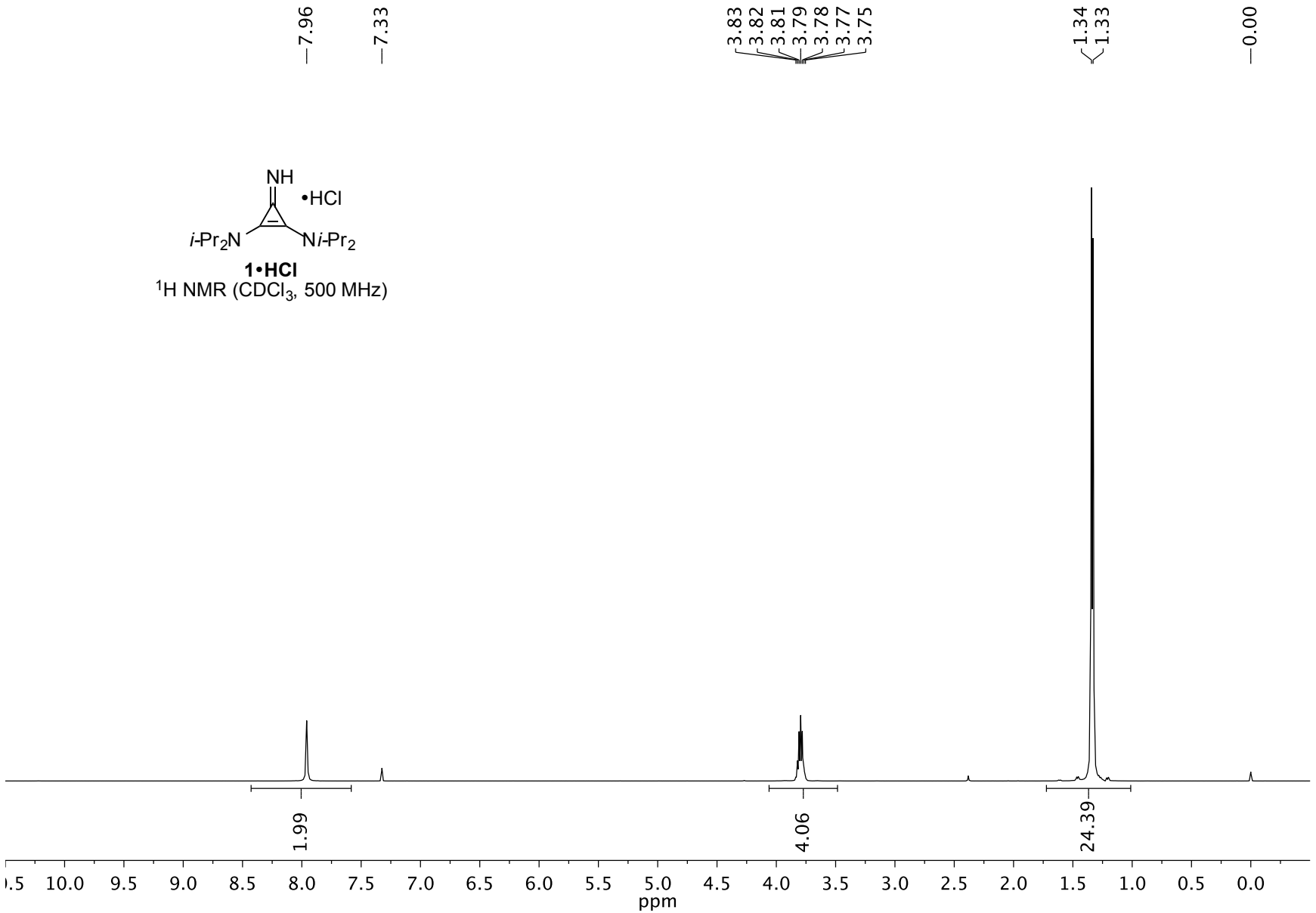

122.74
77.48
77.16
76.84
62.46
Cl
Cl
Cl
Cl
^{13}C NMR ($CDCl_3$,101 MHz)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

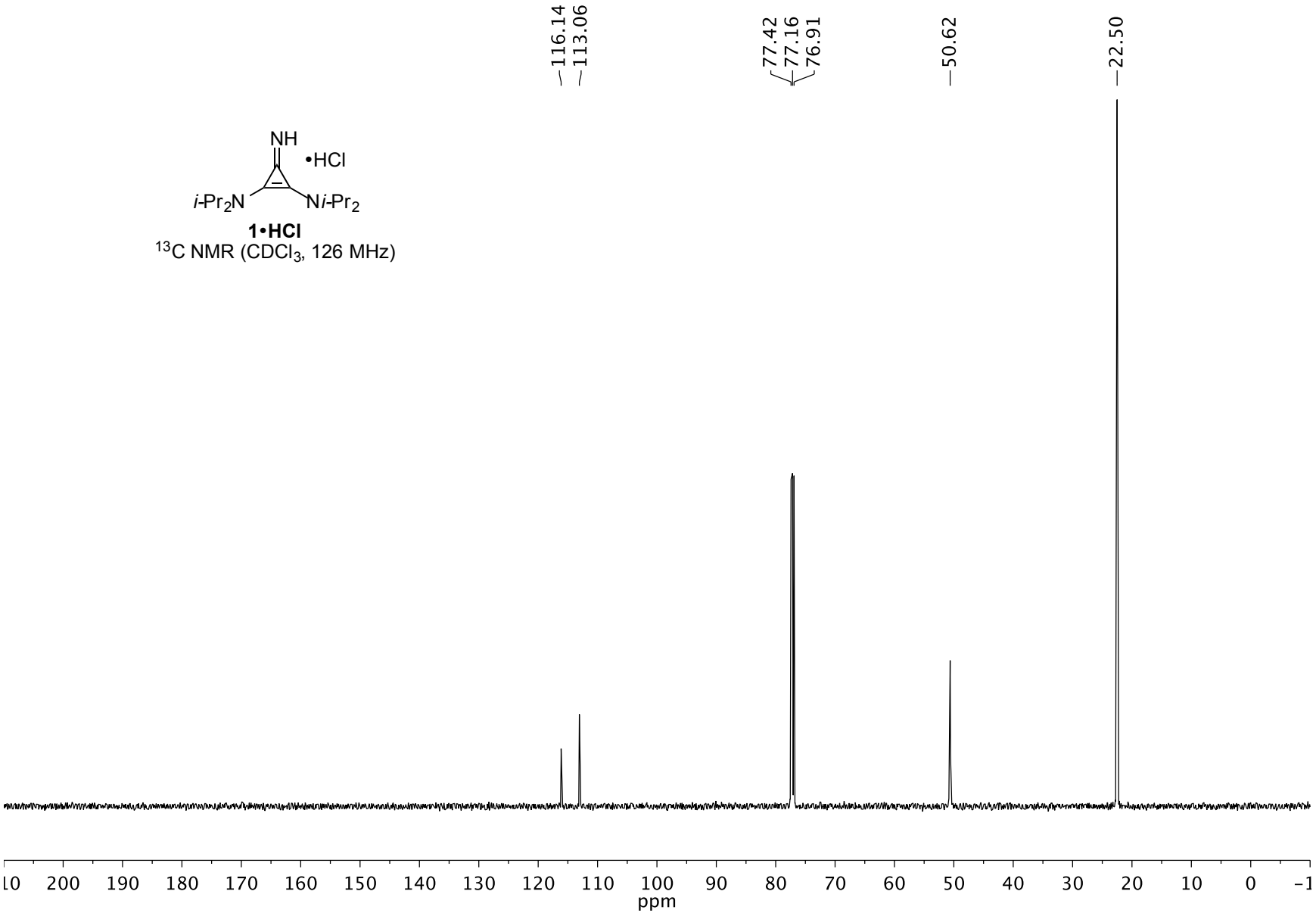

7.30
4.07
4.05
3.11
3.10
3.09
1.61
1.60
0.00
NH •HBF4
P
N
N
N
9•HBF4
1H NMR (CDCl3, 500 MHz)
2.00
12.12
18.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

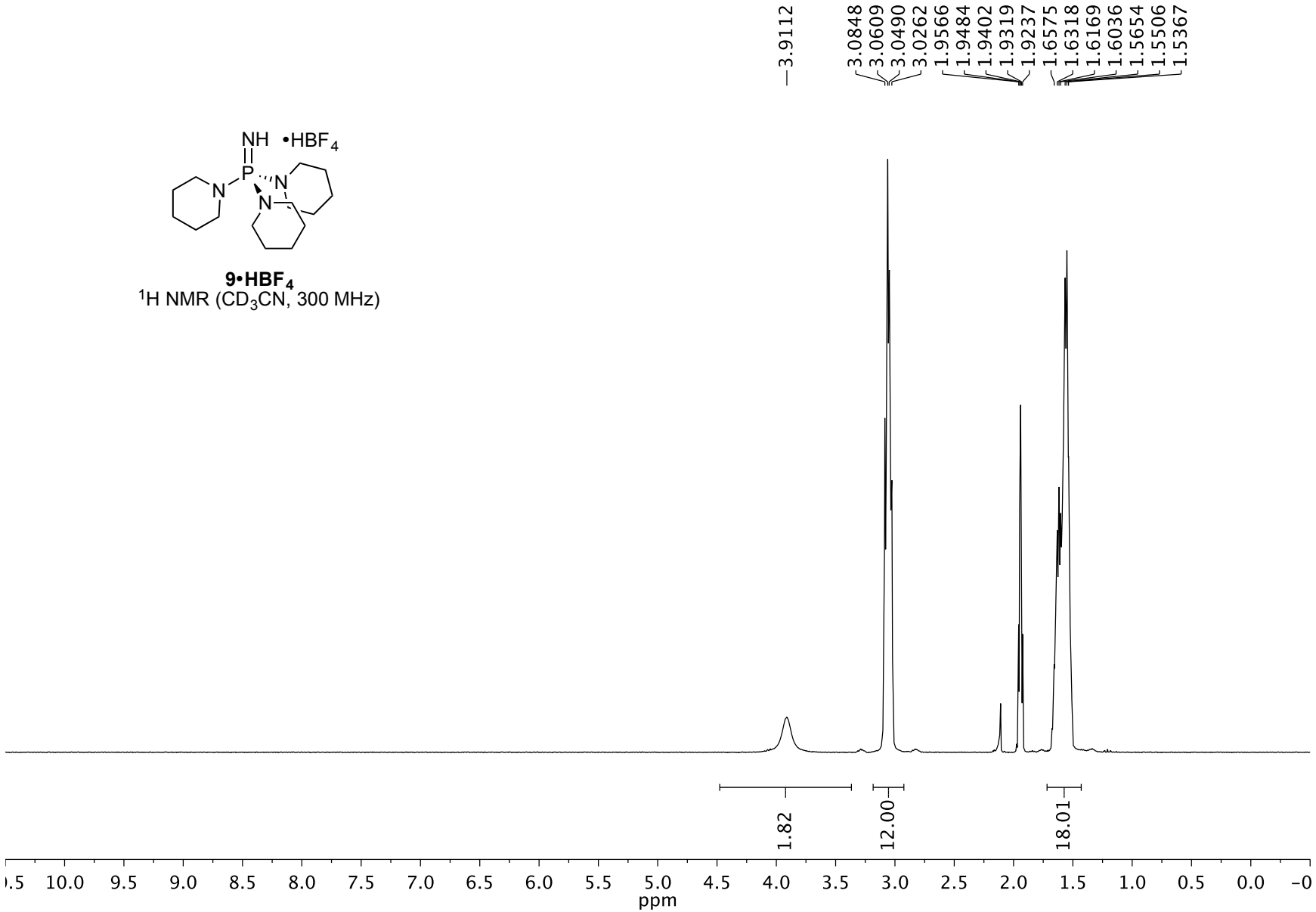


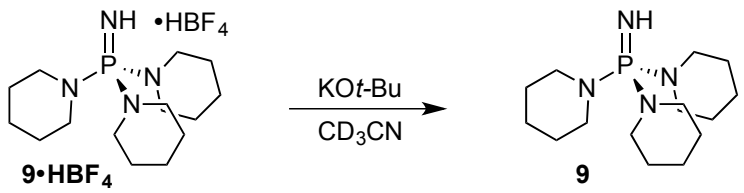
9•HBF$_4$
^{13}C NMR ($CDCl_3$, 126 MHz)


35.38
NH •HBF4
P
N
N
N
9•HBF4
31P NMR (CDCl3, 162 MHz)
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
ppm


7.96
7.33
3.83
3.82
3.81
3.79
3.78
3.77
3.75
1.34
1.33
0.00
NH
•HCl
i-Pr2N
Ni-Pr2
1•HCl
1H NMR (CDCl3, 500 MHz)
1.99
4.06
24.39
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

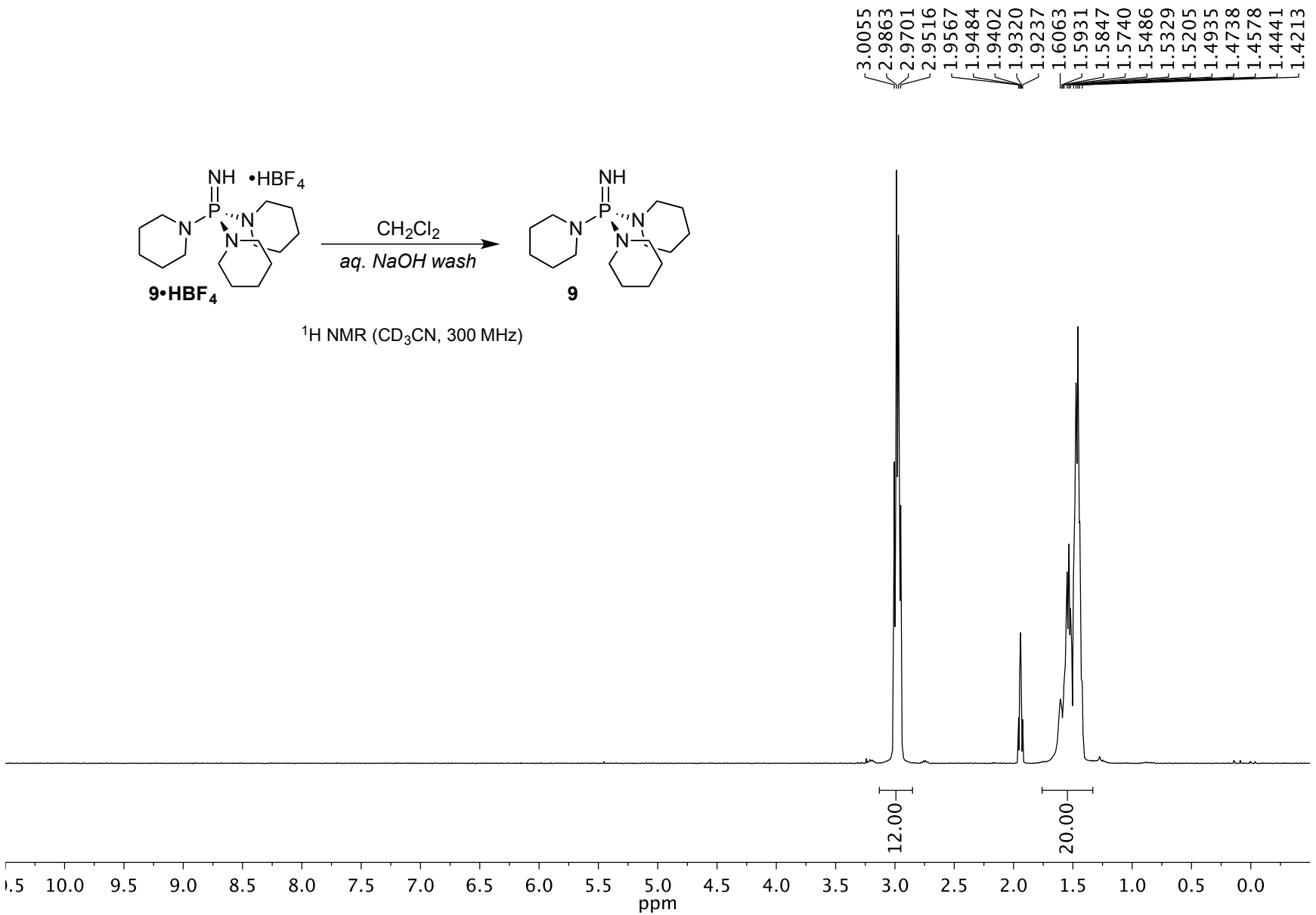

NH
•HCl
i-Pr2N
Ni-Pr2
1•HCl
13C NMR (CDCl3, 126 MHz)
116.14
113.06
77.42
77.16
76.91
50.62
22.50
ppm

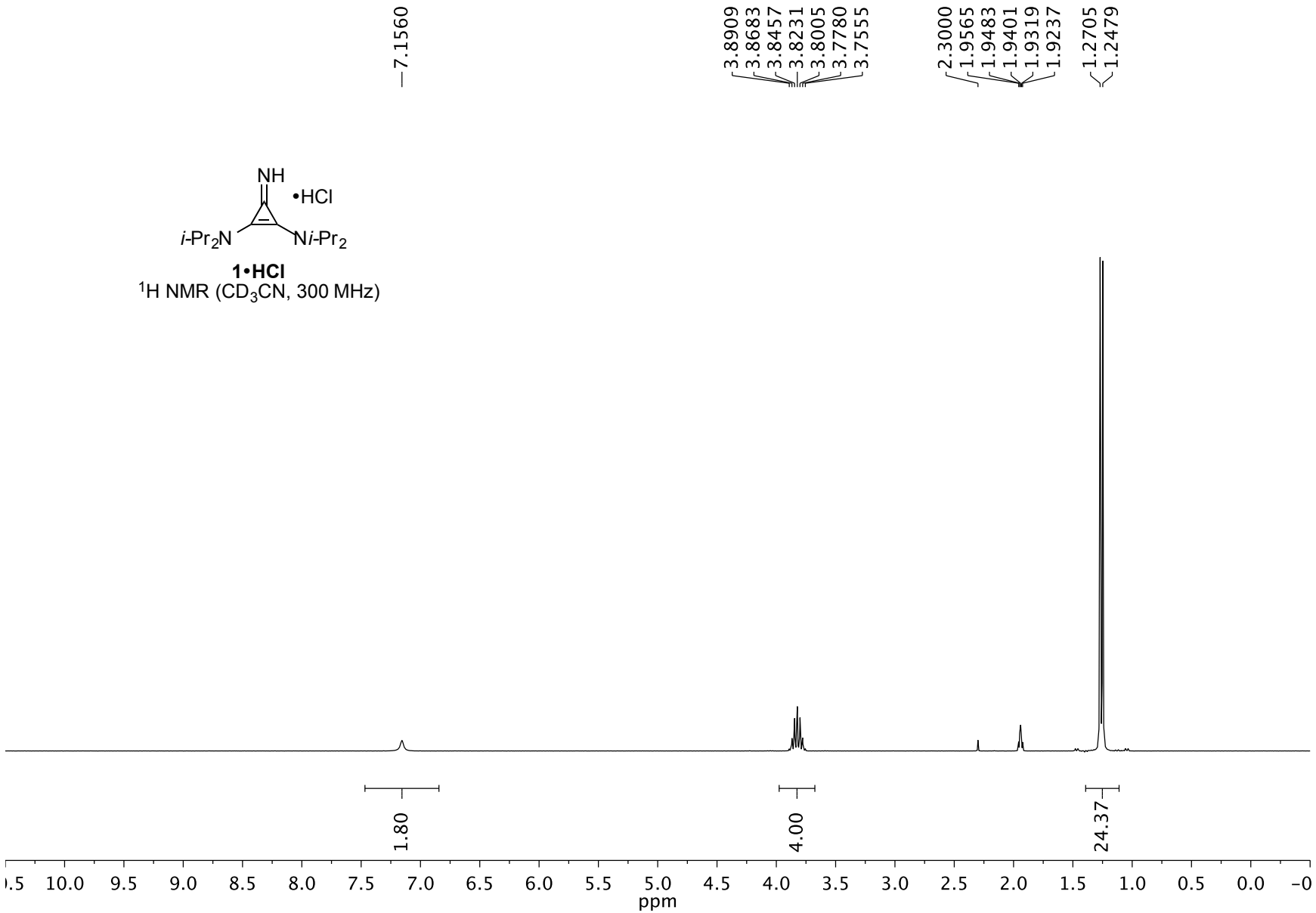

NH •HBF4
P
N
N
N
9•HBF4
1H NMR (CD3CN, 300 MHz)
3.9112
3.0848
3.0609
3.0490
3.0262
1.9566
1.9484
1.9402
1.9319
1.9237
1.6575
1.6318
1.6169
1.6036
1.5654
1.5506
1.5367
1.82
12.00
18.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

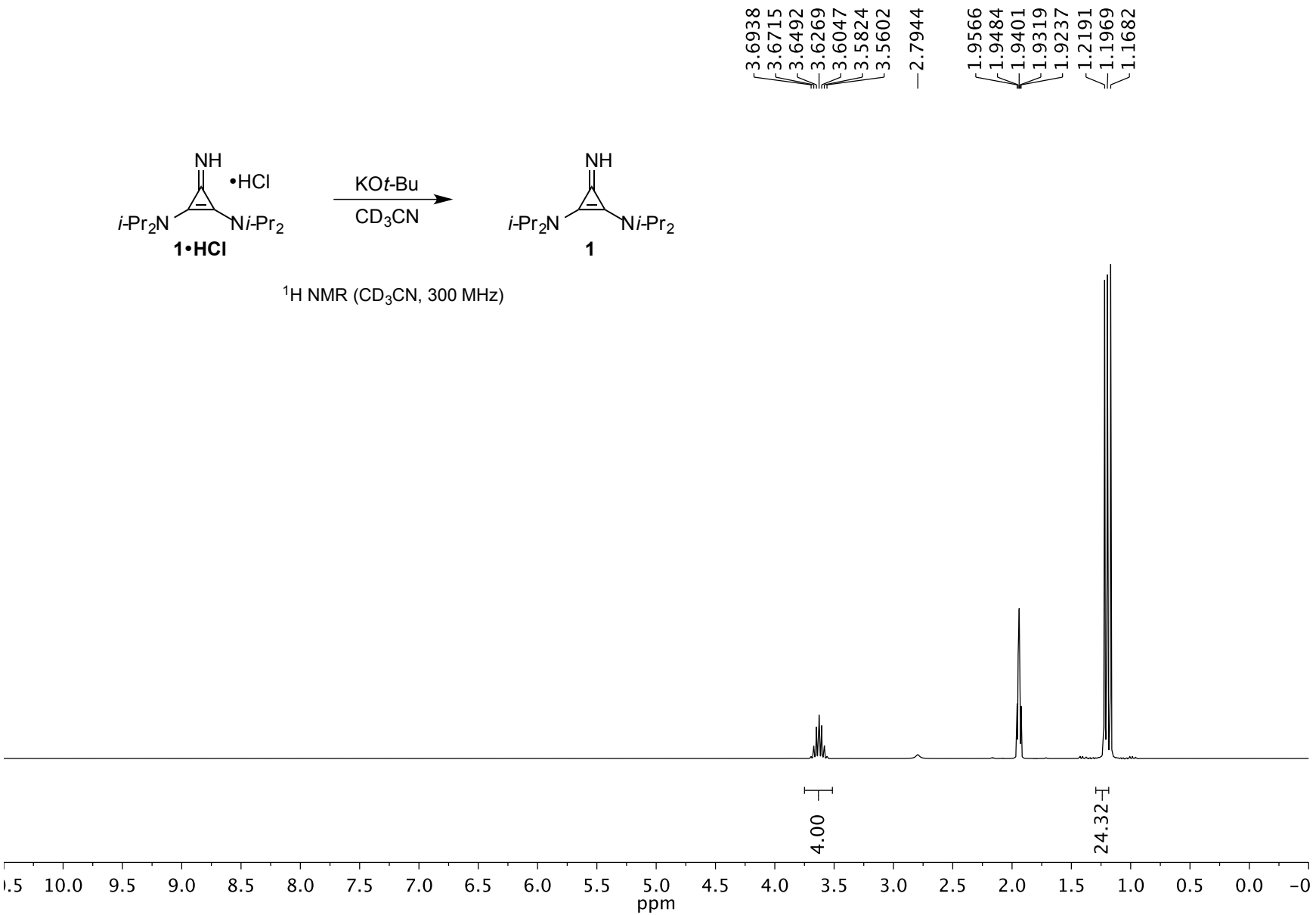


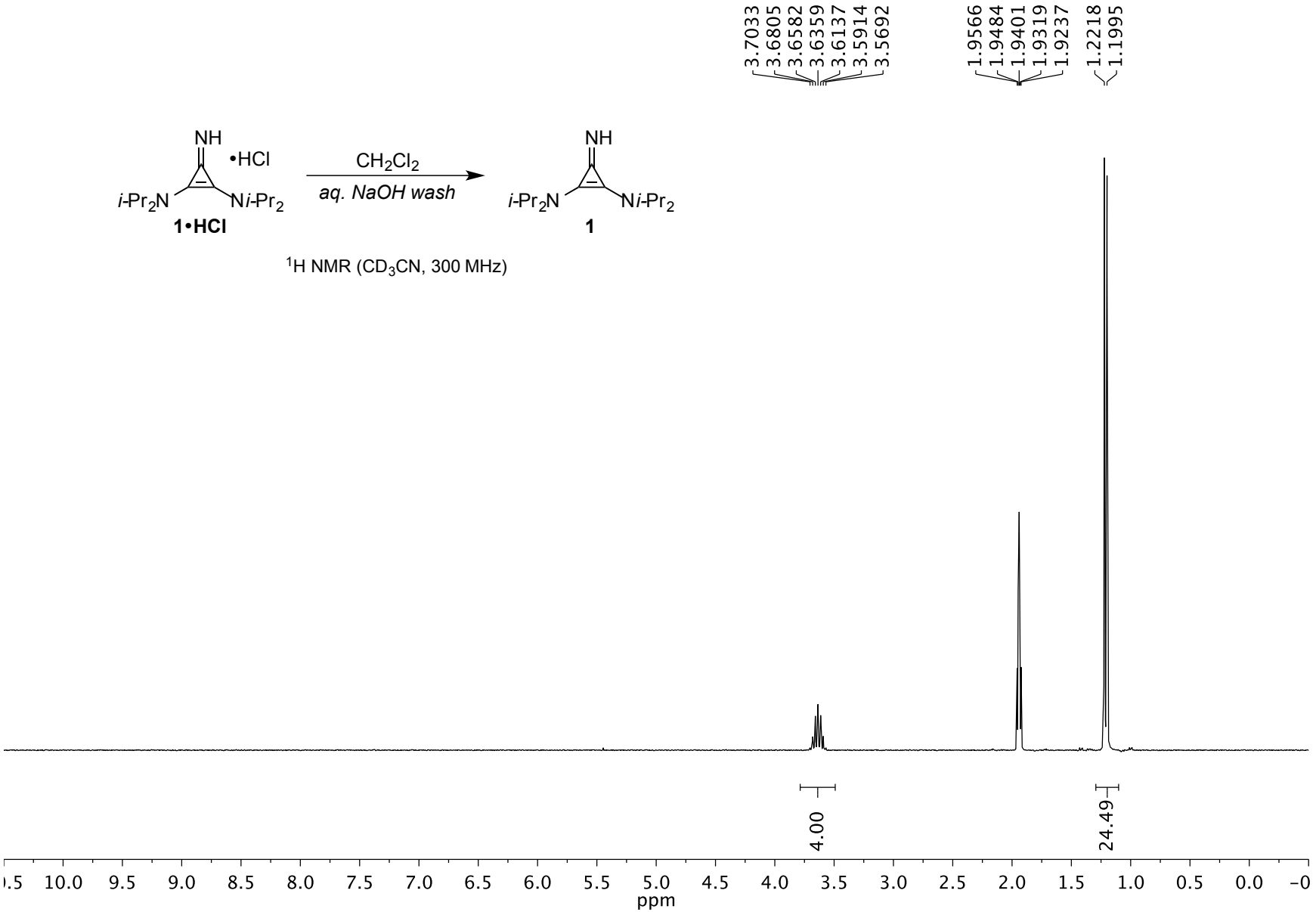
9•HBF$_4$ **9**

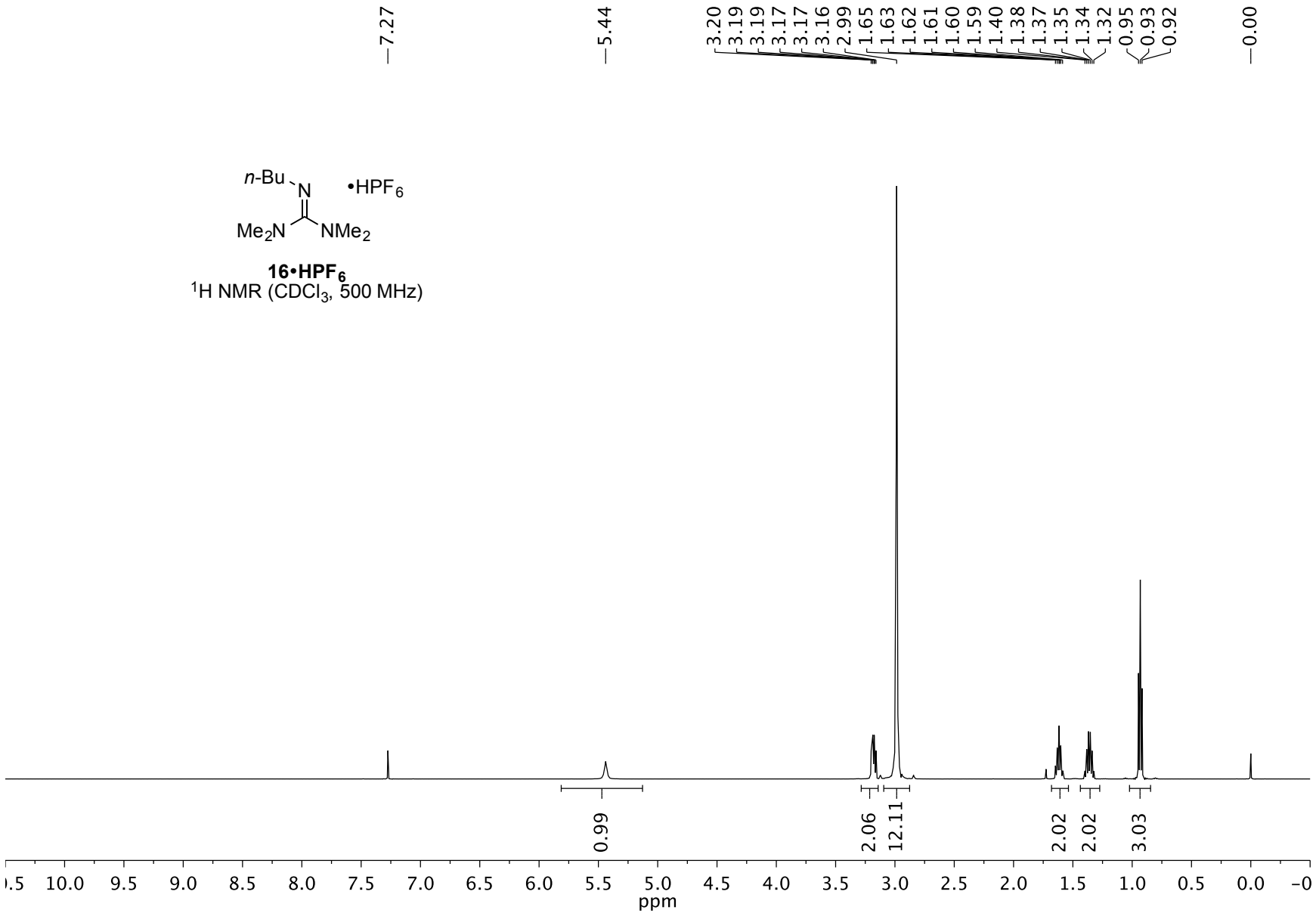
^{1}H NMR (CD_3CN, 300 MHz)

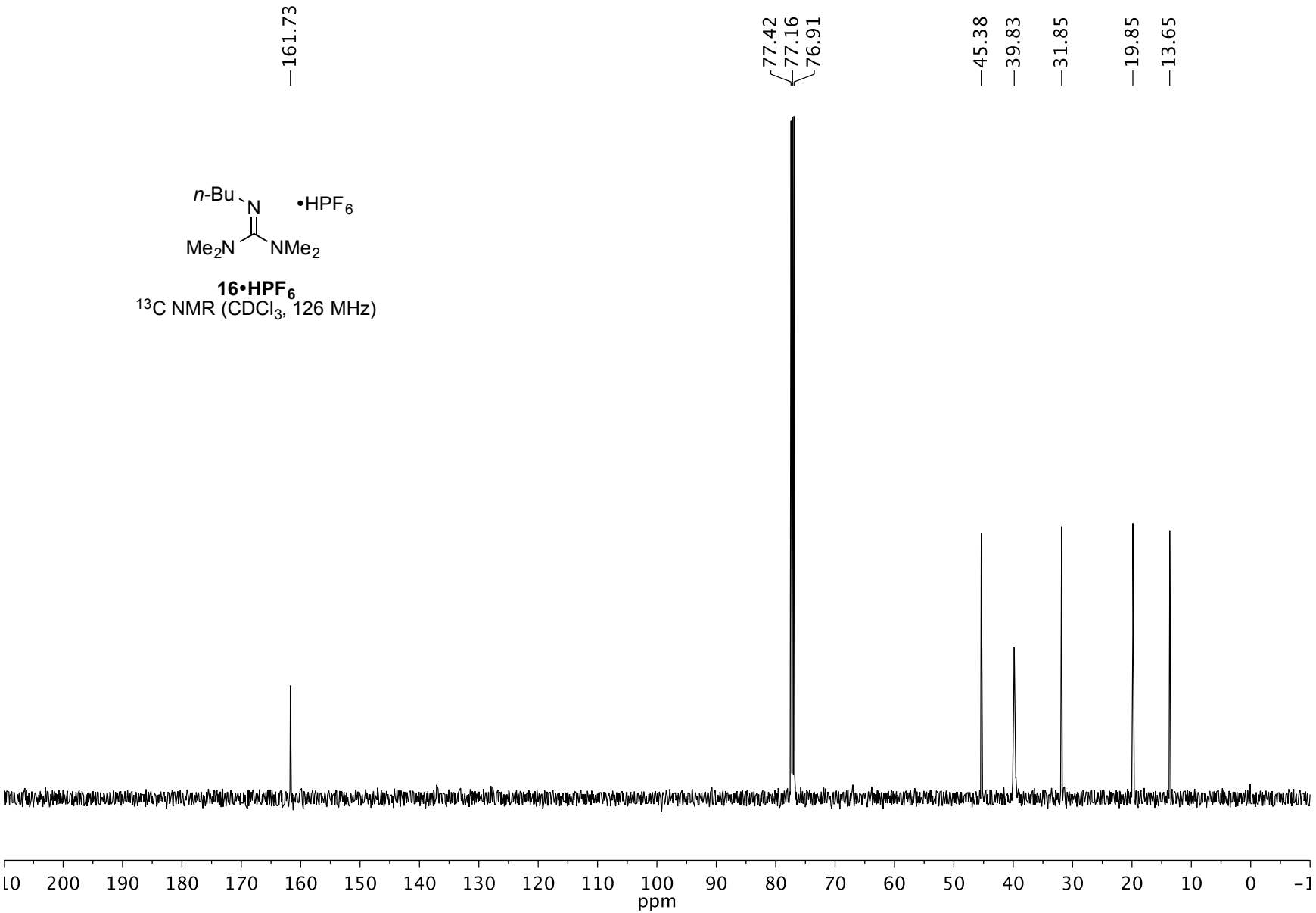

3.0055
2.9863
2.9701
2.9516
1.9567
1.9484
1.9402
1.9320
1.9237
1.6063
1.5931
1.5847
1.5740
1.5486
1.5329
1.5205
1.4935
1.4738
1.4578
1.4441
1.4213
NH •HBF4
P
N
N
N
CH2Cl2
aq. NaOH wash
NH
P
N
N
N
9•HBF4
9
1H NMR (CD3CN, 300 MHz)
12.00
20.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

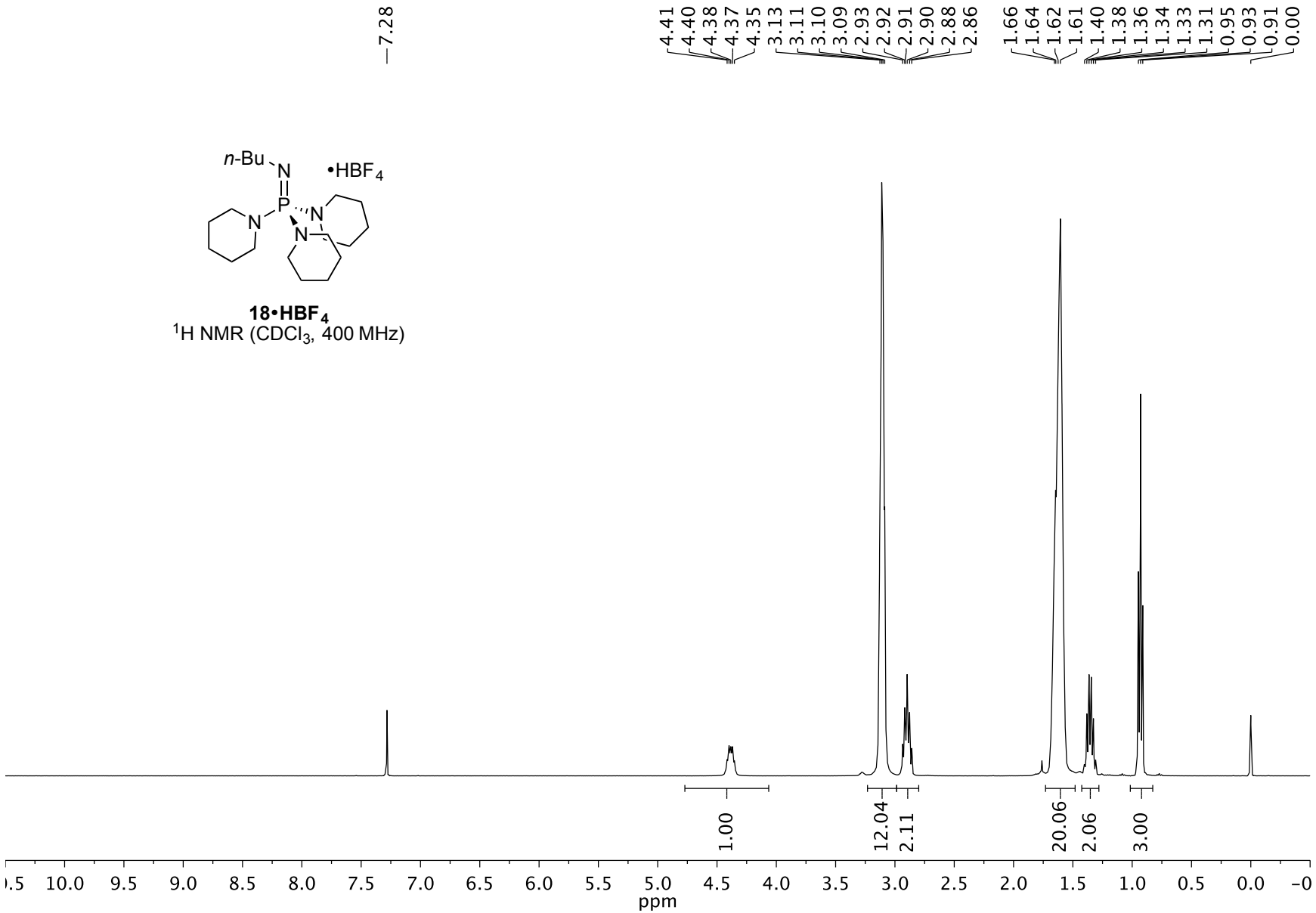

7.1560
3.8909
3.8683
3.8457
3.8231
3.8005
3.7780
3.7555
2.3000
1.9565
1.9483
1.9401
1.9319
1.9237
1.2705
1.2479
NH
•HCl
i-Pr2N
Ni-Pr2
1•HCl
1H NMR (CD3CN, 300 MHz)
1.80
4.00
24.37
ppm


3.6938
3.6715
3.6492
3.6269
3.6047
3.5824
3.5602
2.7944
1.9566
1.9484
1.9401
1.9319
1.9237
1.2191
1.1969
1.1682
NH
•HCl
i-Pr2N
Ni-Pr2
1•HCl
KOt-Bu
CD3CN
NH
i-Pr2N
Ni-Pr2
1
1H NMR (CD3CN, 300 MHz)
4.00
24.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

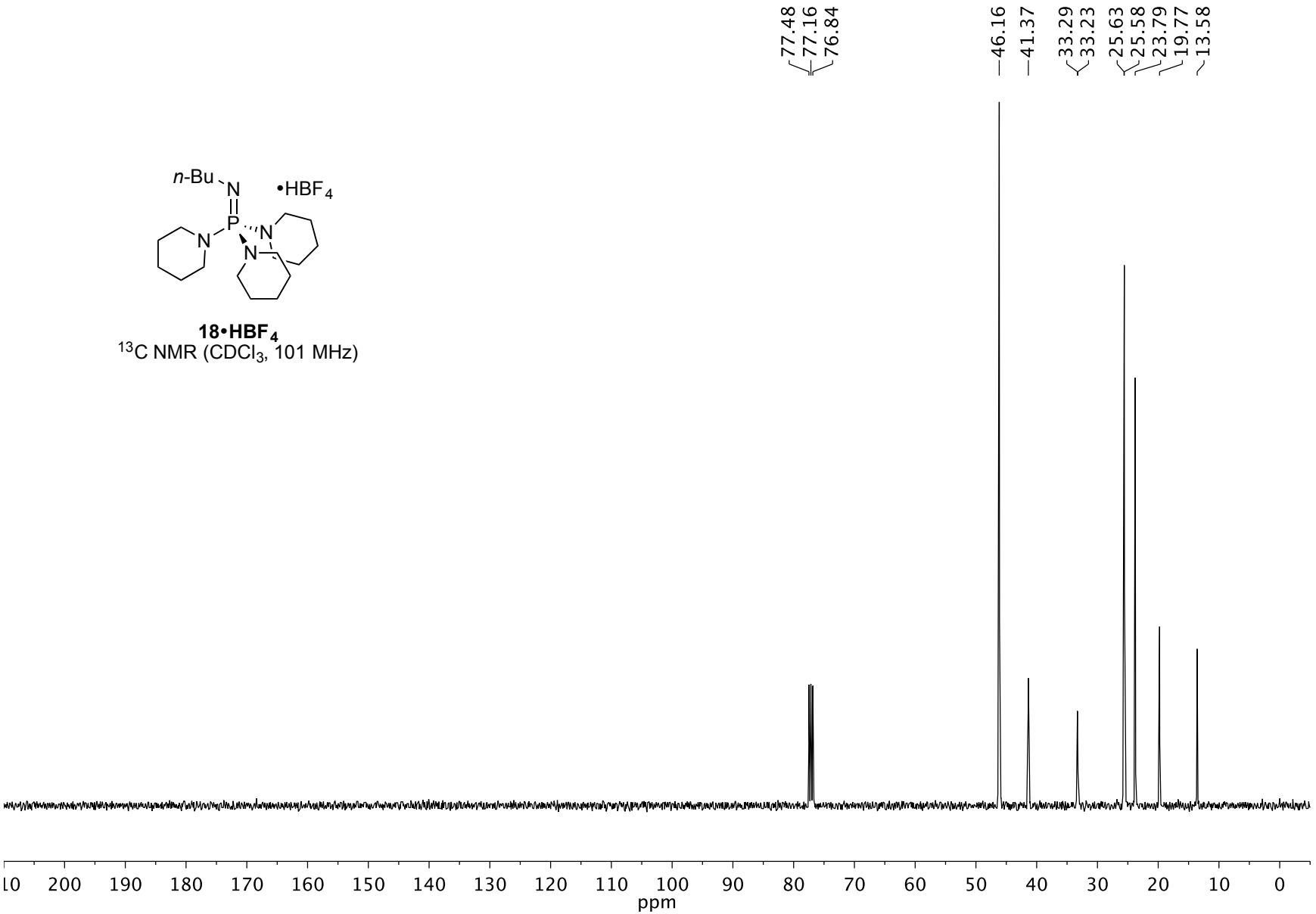

3.7033
3.6805
3.6582
3.6359
3.6137
3.5914
3.5692
1.9566
1.9484
1.9401
1.9319
1.9237
1.2218
1.1995
NH
•HCl
i-Pr2N
Ni-Pr2
1•HCl
CH2Cl2
aq. NaOH wash
NH
i-Pr2N
Ni-Pr2
1
1H NMR (CD3CN, 300 MHz)
4.00
24.49
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


7.27
5.44
3.20
3.19
3.19
3.17
3.17
3.16
2.99
1.65
1.63
1.62
1.61
1.60
1.59
1.40
1.38
1.37
1.35
1.34
1.32
0.95
0.93
0.92
0.00
n-Bu
N
•HPF6
Me2N
NMe2
16•HPF6
1H NMR (CDCl3, 500 MHz)
0.99
2.06
12.11
2.02
2.02
3.03
ppm

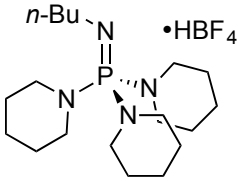

161.73
77.42
77.16
76.91
45.38
39.83
31.85
19.85
13.65
n-Bu
N
•HPF6
Me2N
NMe2
16•HPF6
13C NMR (CDCl3, 126 MHz)
ppm



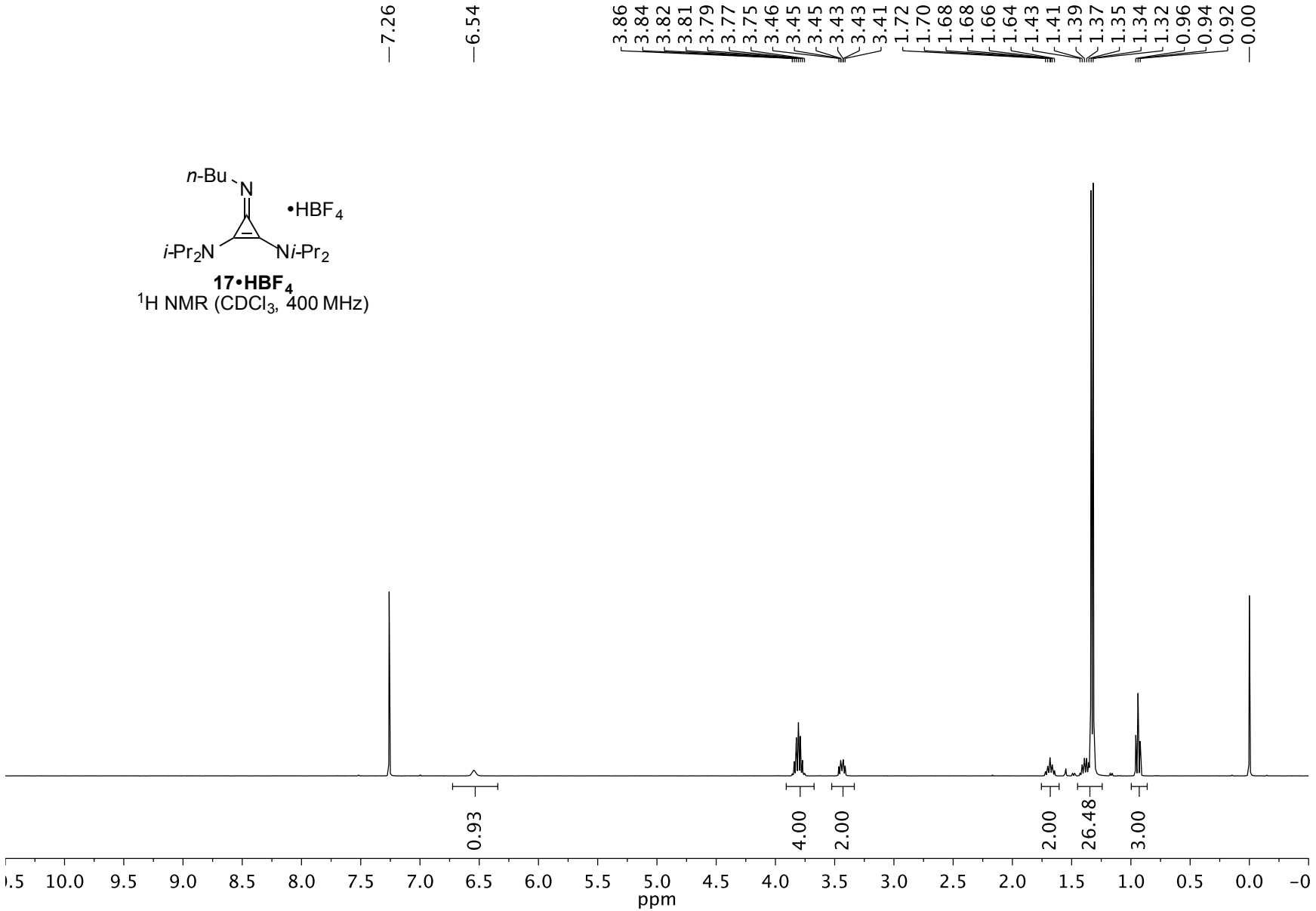
18•HBF$_4$
^{1}H NMR ($CDCl_3$, 400 MHz)

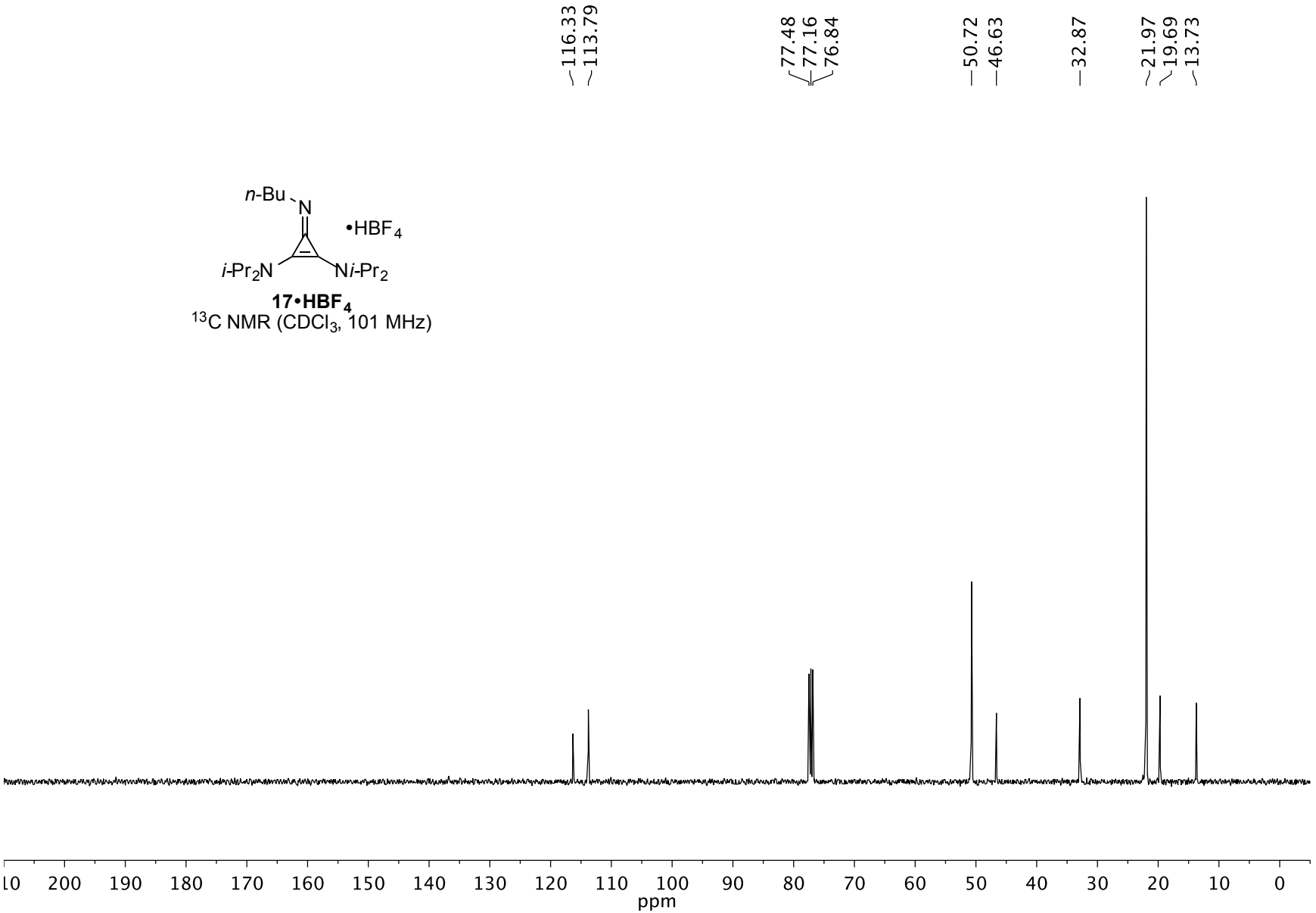


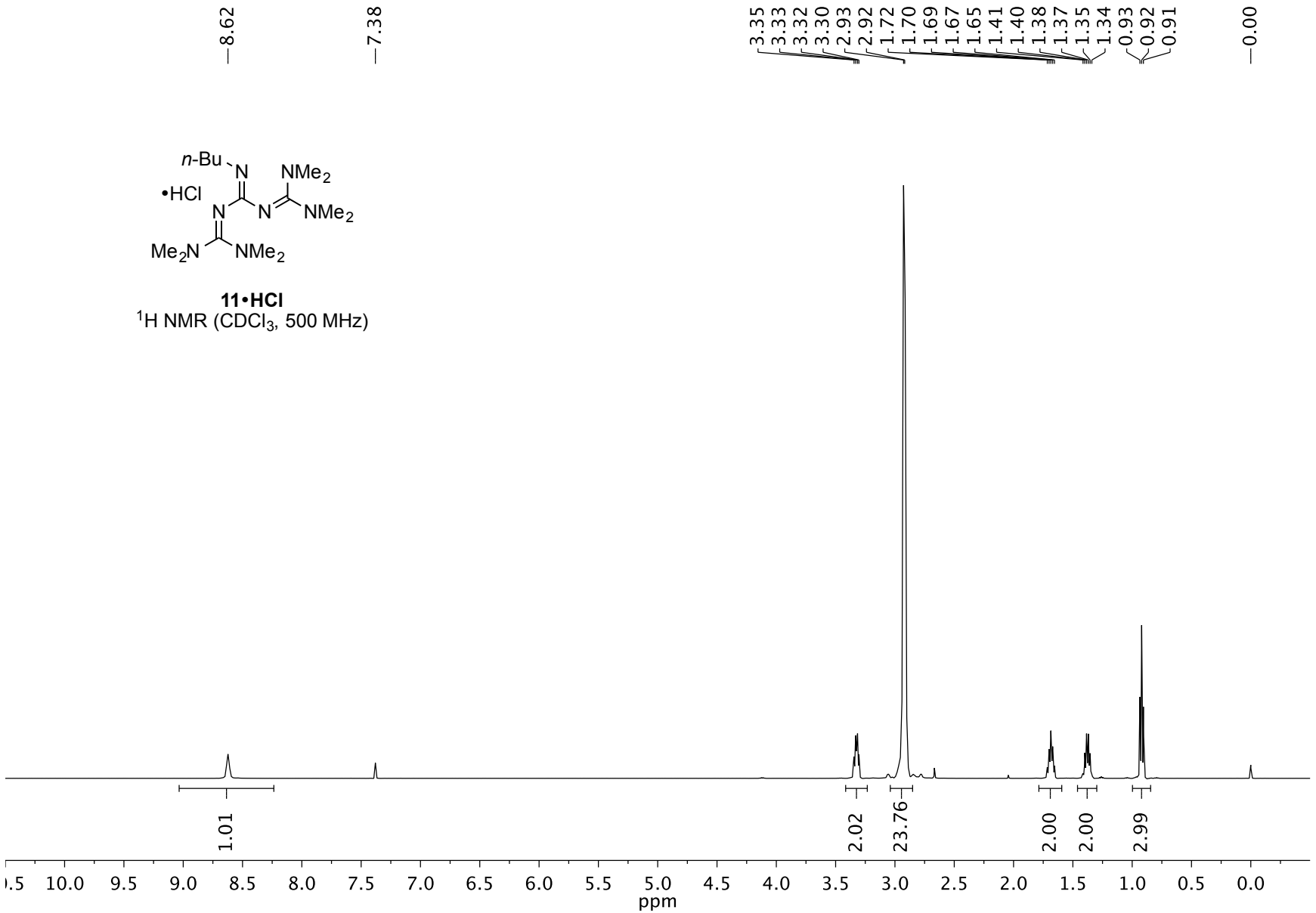
18•HBF$_4$
^{13}C NMR ($CDCl_3$, 101 MHz)

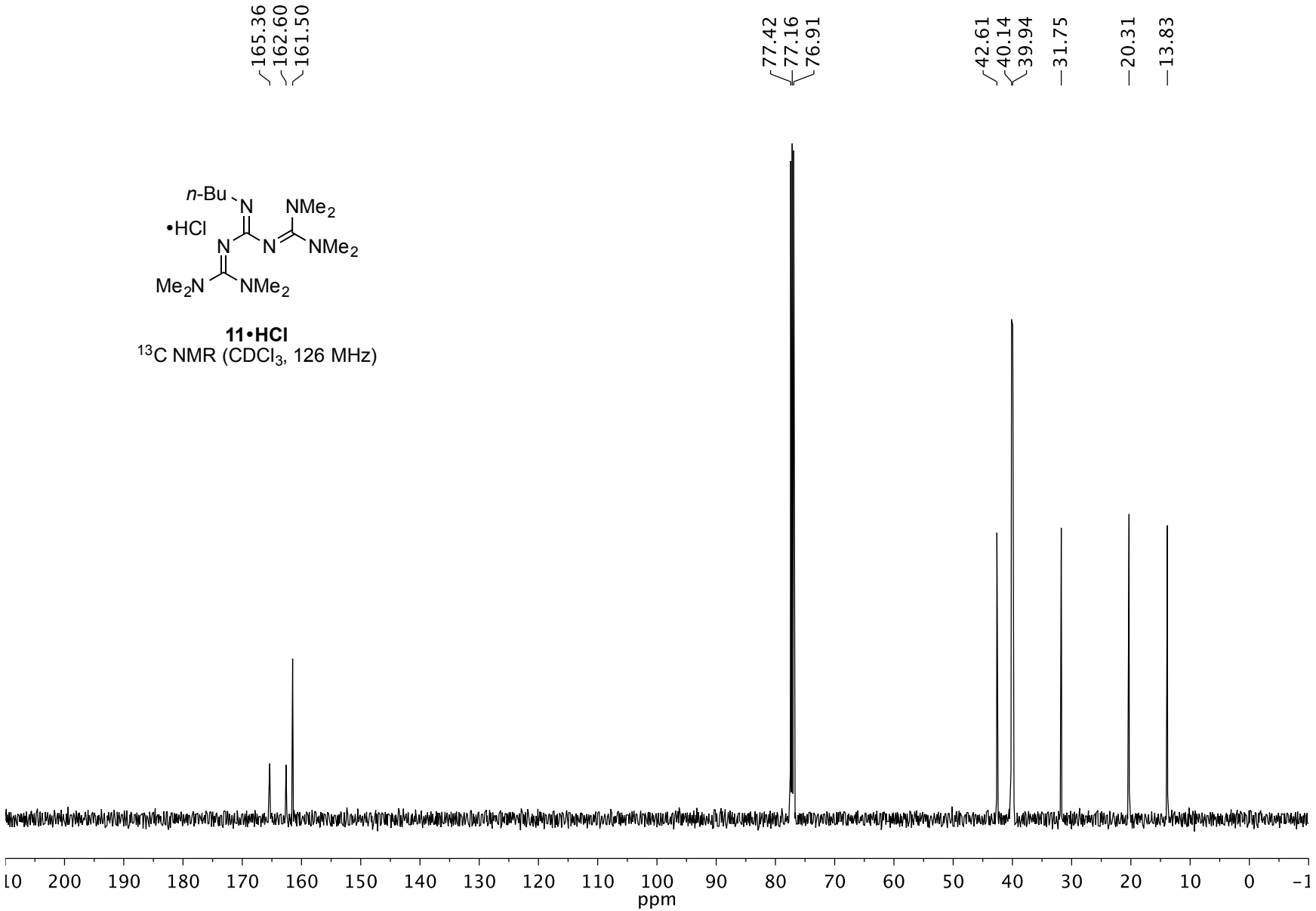


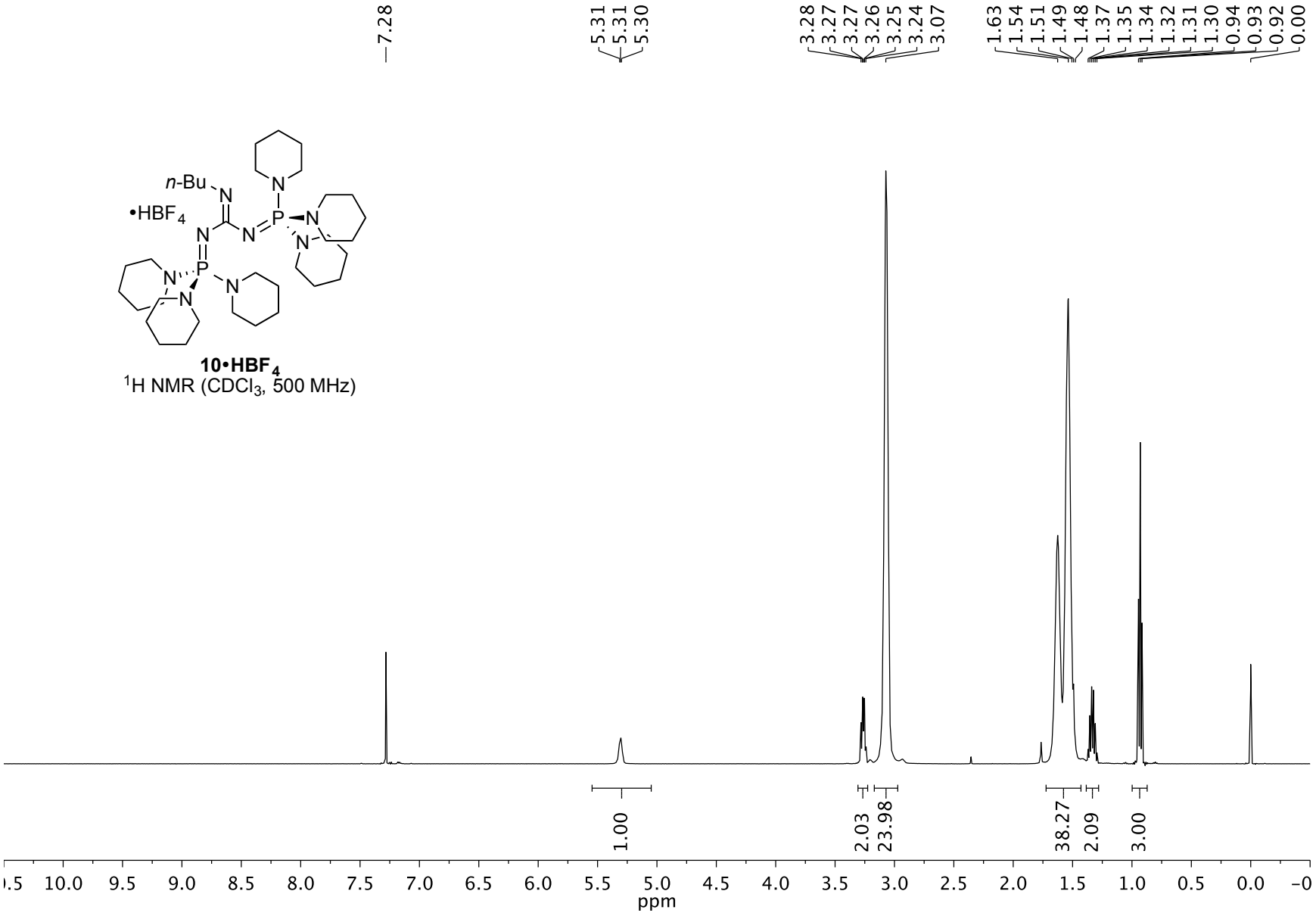
18•HBF$_4$
^{31}P NMR ($CDCl_3$, 162 MHz)

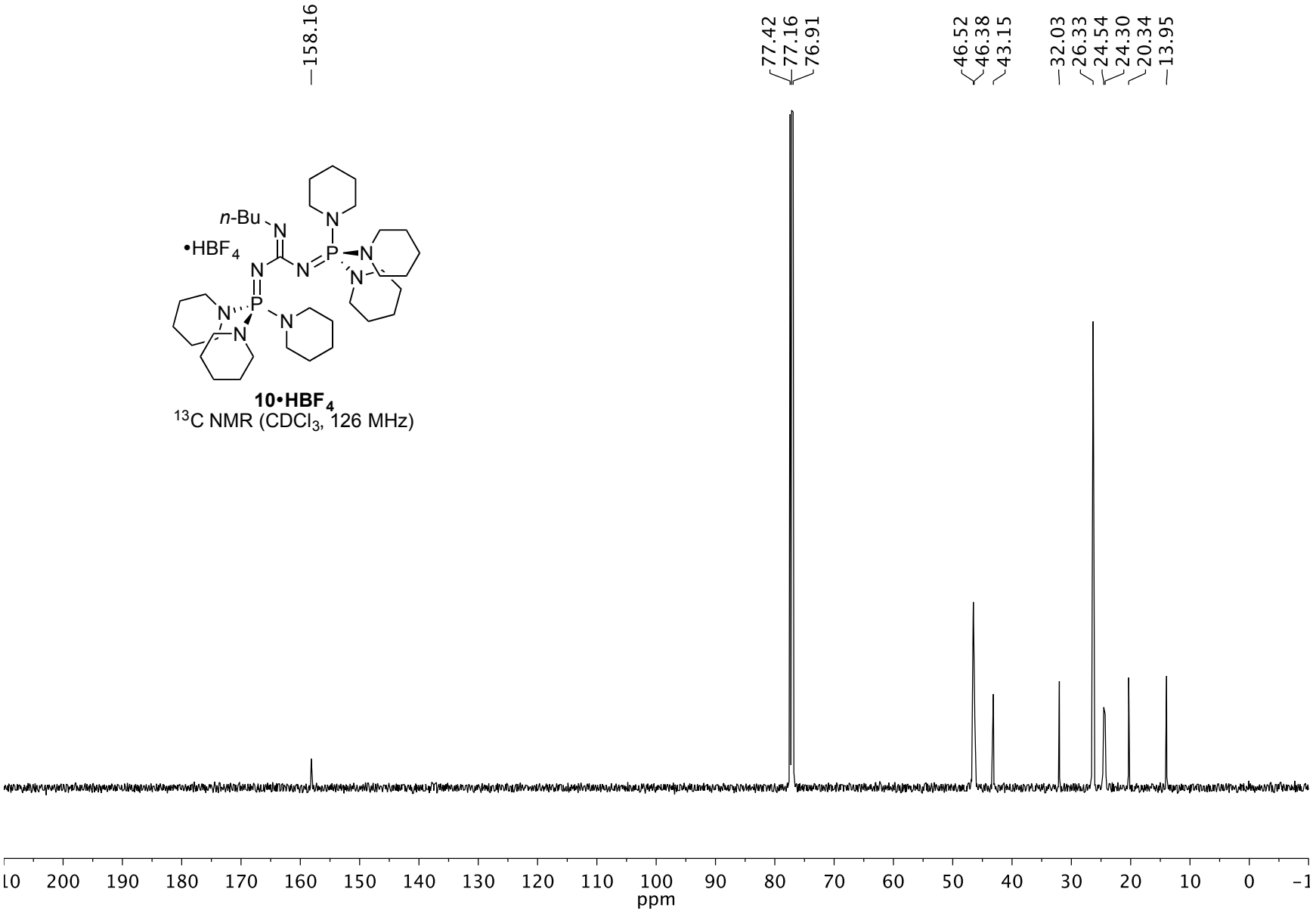

7.26
6.54
3.86
3.84
3.82
3.81
3.79
3.77
3.75
3.46
3.45
3.45
3.43
3.43
3.41
1.72
1.70
1.68
1.68
1.66
1.64
1.43
1.41
1.39
1.37
1.35
1.34
1.32
0.96
0.94
0.92
0.00
n-Bu
N
•HBF4
i-Pr2N
Ni-Pr2
17•HBF4
1H NMR (CDCl3, 400 MHz)
0.93
4.00
2.00
2.00
26.48
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

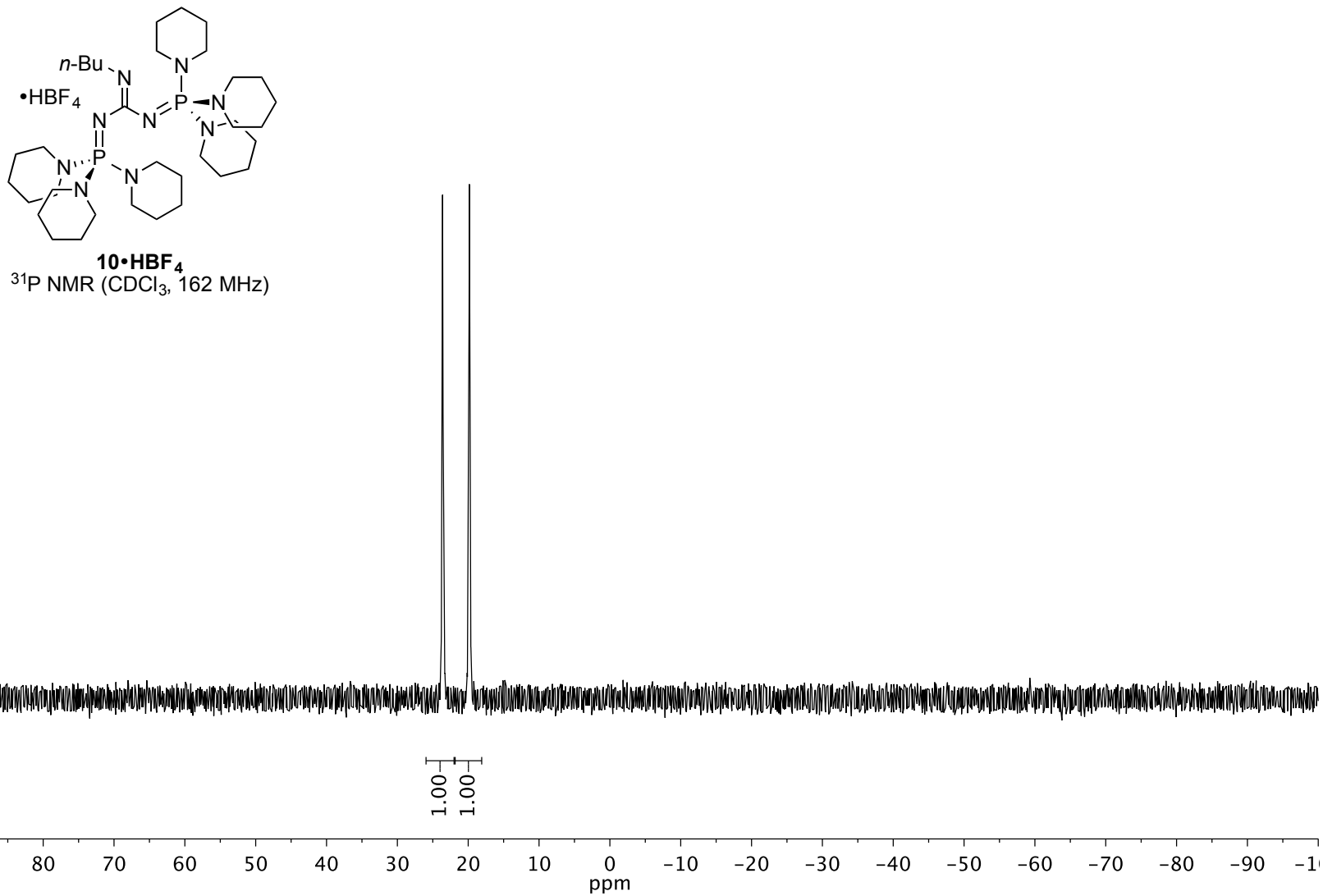

116.33
113.79
77.48
77.16
76.84
50.72
46.63
32.87
21.97
19.69
13.73
n-Bu
N
•HBF4
i-Pr2N
Ni-Pr2
17•HBF4
13C NMR (CDCl3, 101 MHz)
ppm

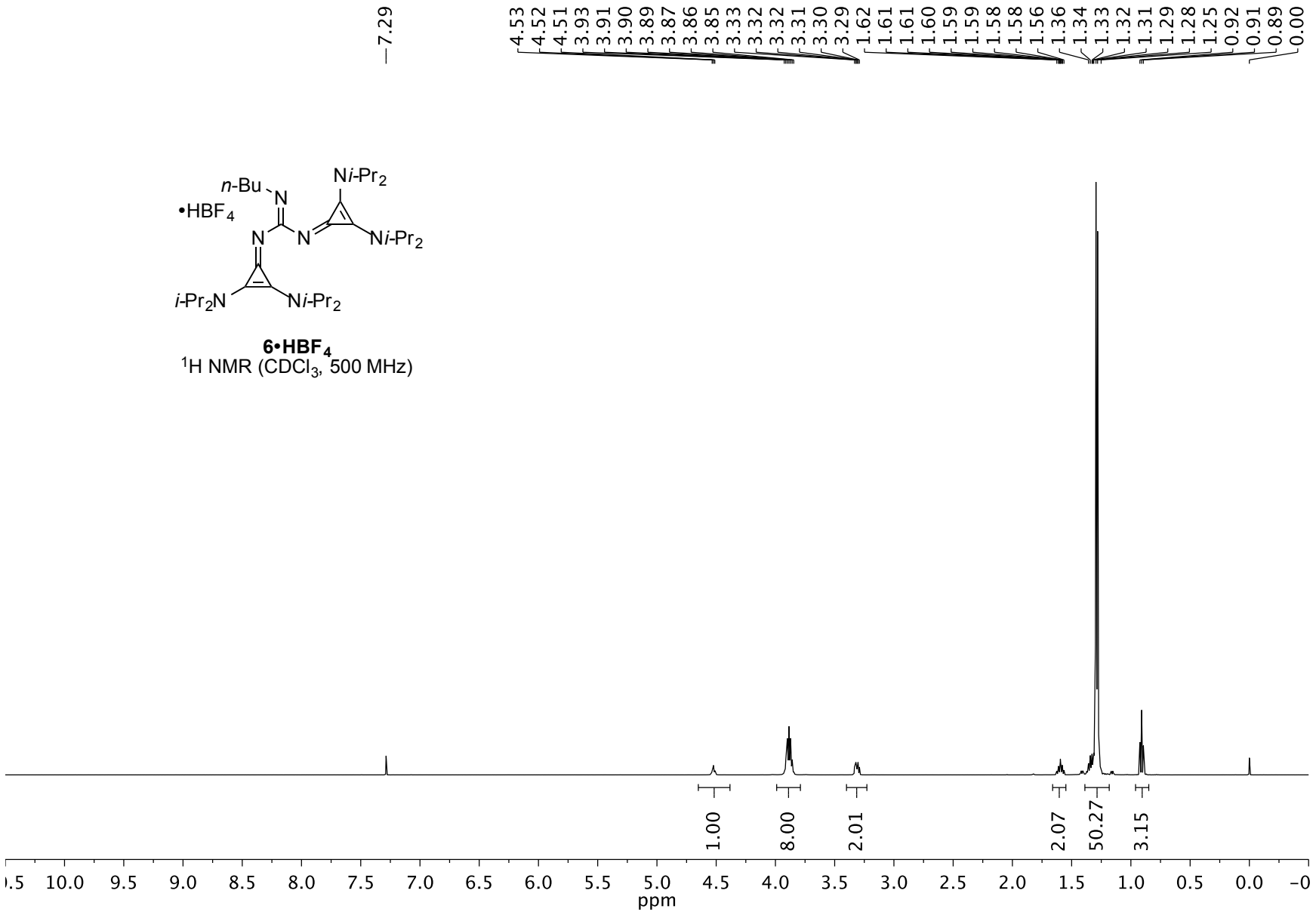

8.62
7.38
3.35
3.33
3.32
3.30
2.93
2.92
1.72
1.70
1.69
1.67
1.65
1.41
1.40
1.38
1.37
1.35
1.34
0.93
0.92
0.91
0.00
n-Bu
N
NMe2
•HCl
N
N
NMe2
Me2N
NMe2
11•HCl
1H NMR (CDCl3, 500 MHz)
1.01
2.02
23.76
2.00
2.00
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


165.36
162.60
161.50
77.42
77.16
76.91
42.61
40.14
39.94
31.75
20.31
13.83
n-Bu
N
NMe2
•HCl
N
N
NMe2
Me2N
NMe2
11•HCl
13C NMR (CDCl3, 126 MHz)
ppm

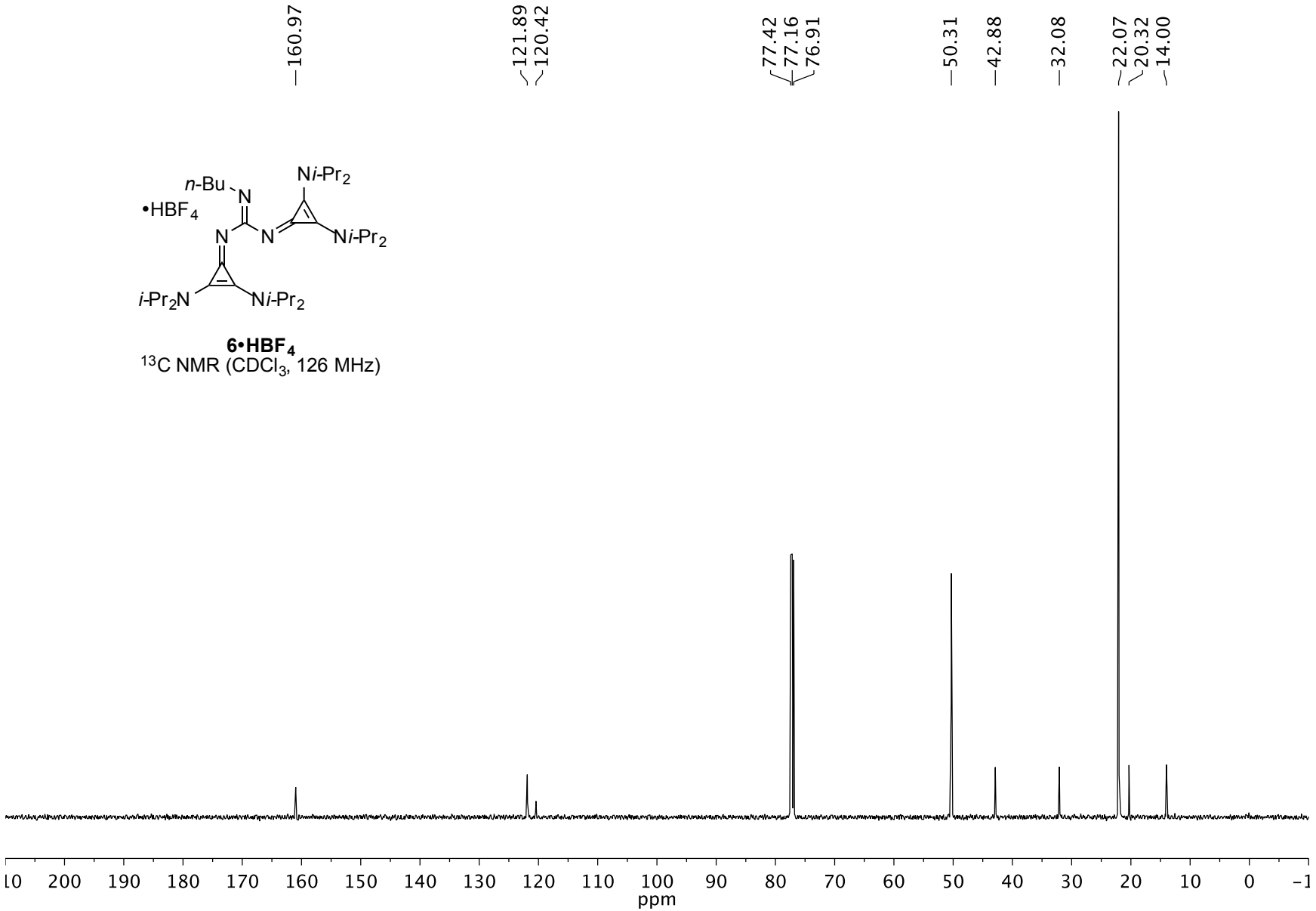

7.28
5.31
5.31
5.30
3.28
3.27
3.27
3.26
3.25
3.24
3.07
1.63
1.54
1.51
1.49
1.48
1.37
1.35
1.34
1.32
1.31
1.30
0.94
0.93
0.92
0.00
n-Bu
•HBF4
10•HBF4
1H NMR (CDCl3, 500 MHz)
1.00
2.03
23.98
38.27
2.09
3.00
ppm


158.16
77.42
77.16
76.91
46.52
46.38
43.15
32.03
26.33
24.54
24.30
20.34
13.95
n-Bu
•HBF4
10•HBF4
13C NMR (CDCl3, 126 MHz)
ppm

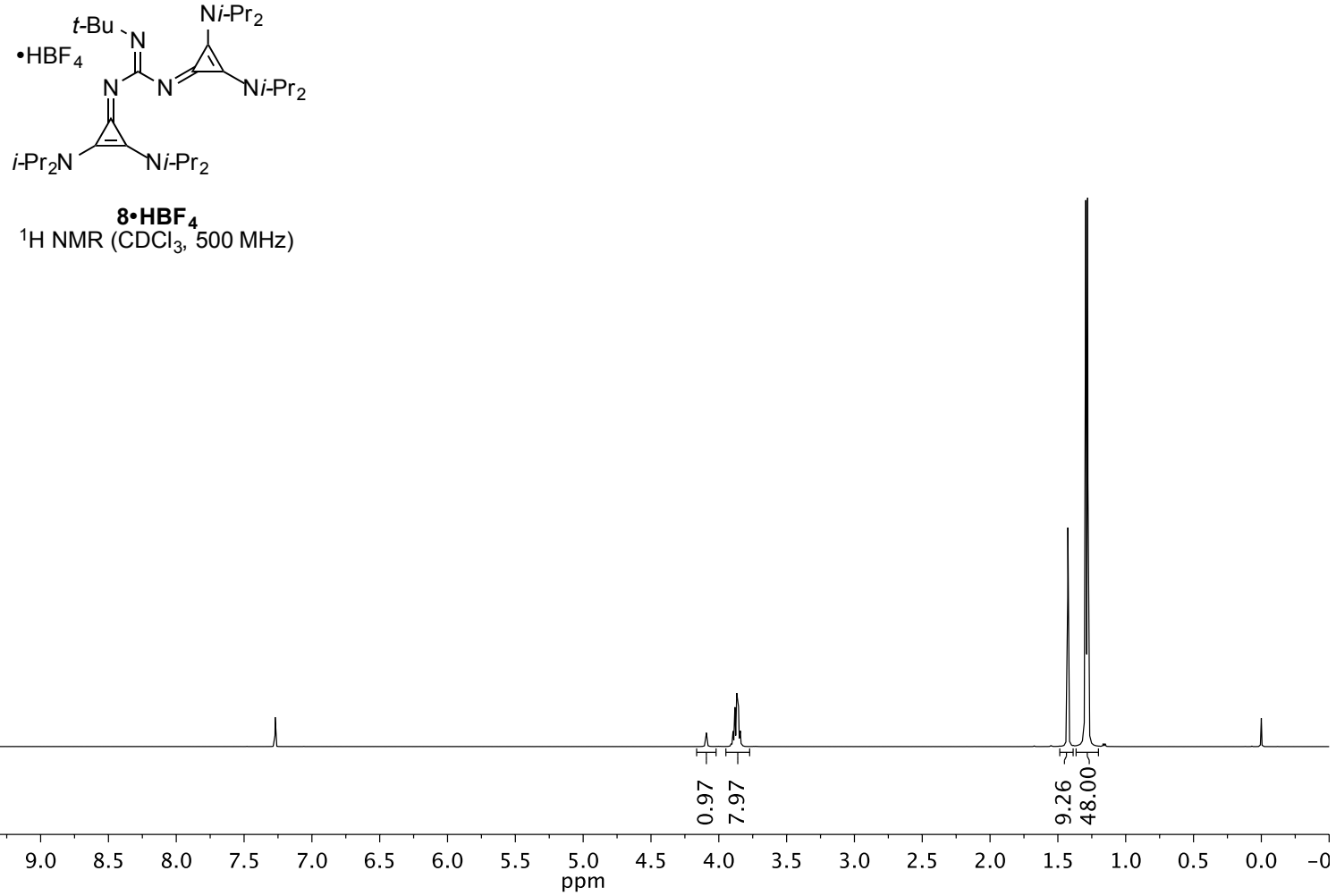

23.62
19.84
n-Bu
•HBF4
10•HBF4
31P NMR (CDCl3, 162 MHz)
1.00
1.00
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
ppm

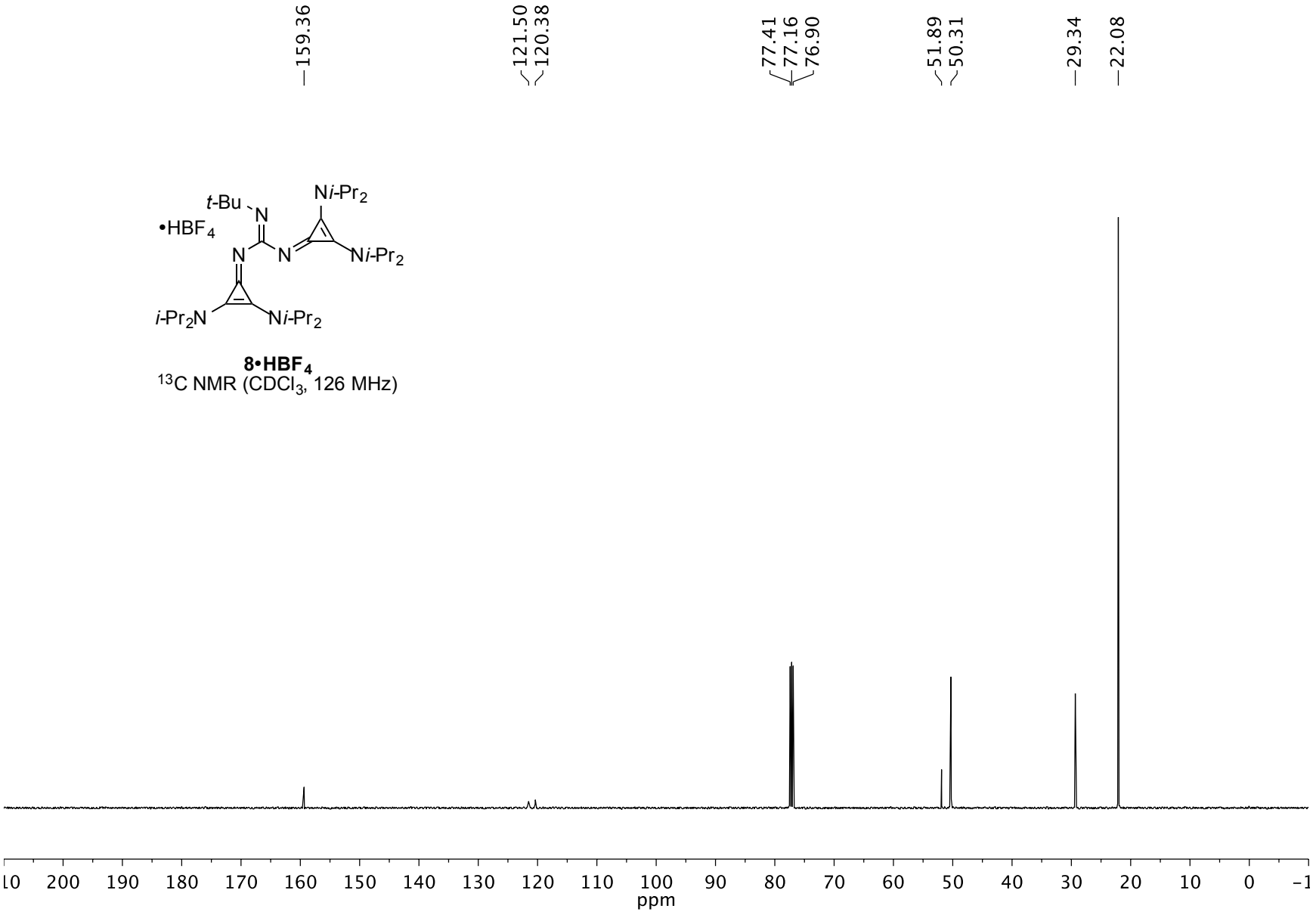


6•HBF$_4$
^{1}H NMR ($CDCl_3$, 500 MHz)

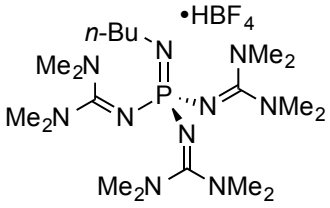


6•HBF$_4$
^{13}C NMR ($CDCl_3$, 126 MHz)

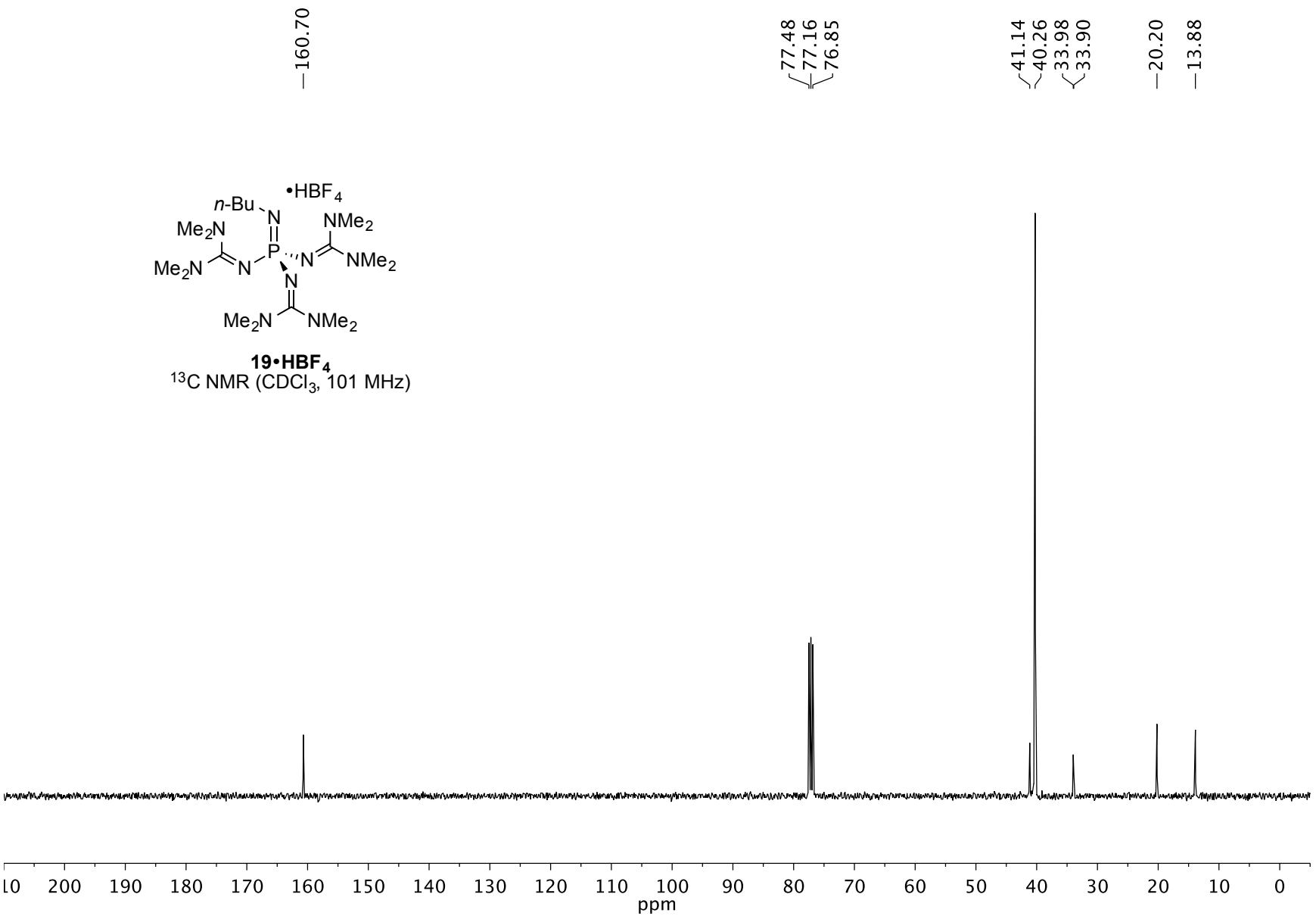

7.27
4.09
3.91
3.90
3.88
3.87
3.85
3.84
3.83
1.43
1.29
1.28
0.00
t-Bu
N
•HBF4
N
N
Ni-Pr2
Ni-Pr2
i-Pr2N
Ni-Pr2
8•HBF4
1H NMR (CDCl3, 500 MHz)
0.97
7.97
9.26
48.00
ppm



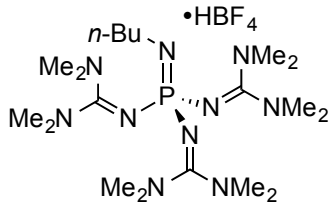
8•HBF$_4$
^{13}C NMR ($CDCl_3$, 126 MHz)



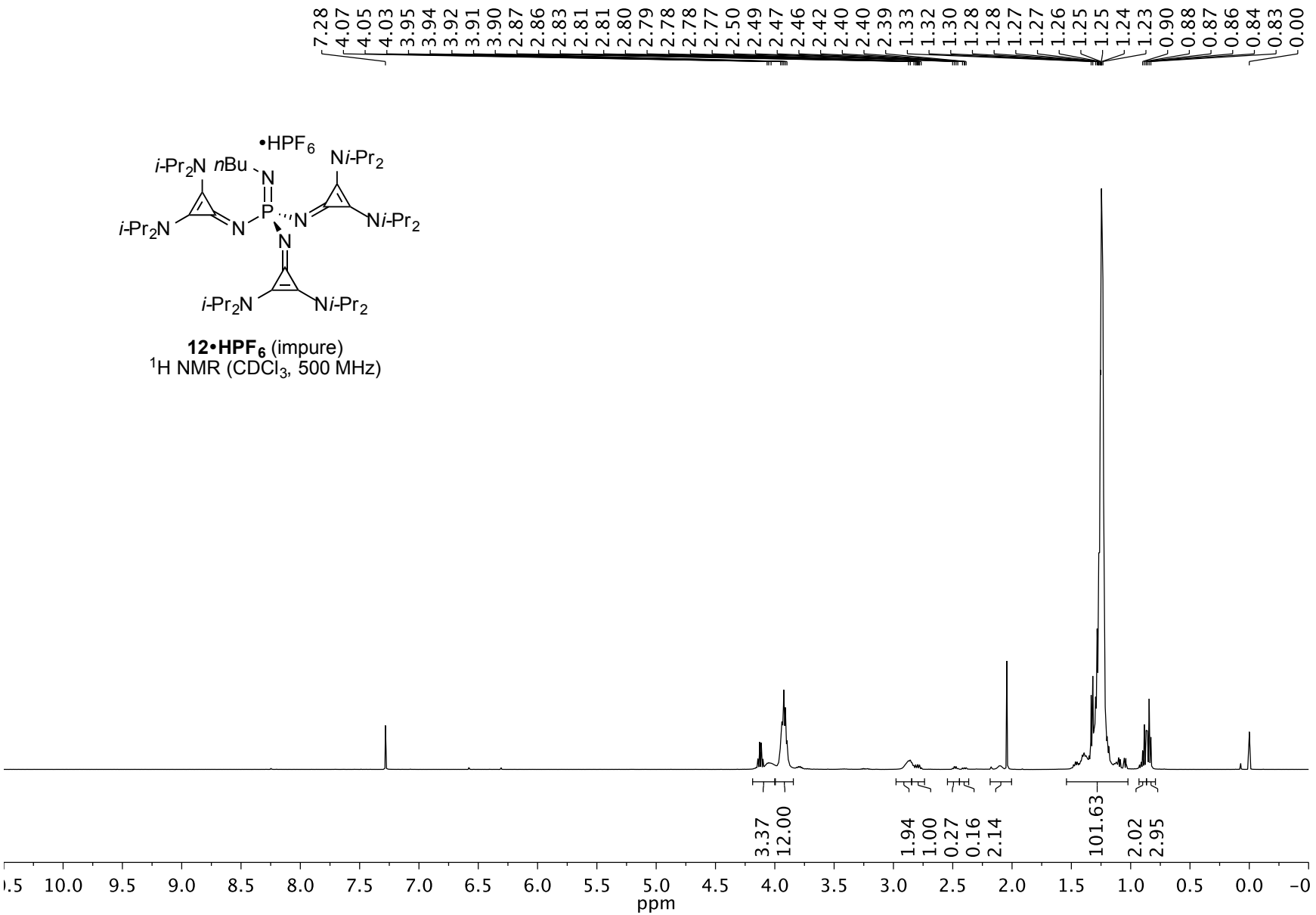
19•HBF$_4$
^{1}H NMR ($CDCl_3$, 400 MHz)

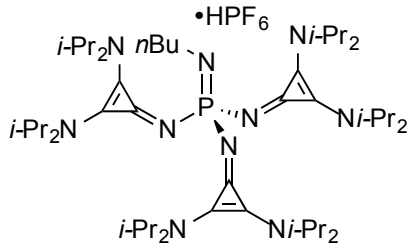


19•HBF$_4$
^{13}C NMR ($CDCl_3$, 101 MHz)



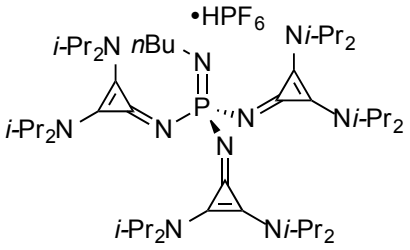
19•HBF$_4$
^{31}P NMR ($CDCl_3$, 162 MHz)


7.28
4.07
4.05
4.03
3.95
3.94
3.92
3.91
3.90
2.87
2.86
2.83
2.81
2.81
2.80
2.79
2.78
2.78
2.77
2.50
2.49
2.47
2.46
2.42
2.40
2.40
2.39
1.33
1.32
1.30
1.28
1.28
1.27
1.27
1.26
1.25
1.25
1.24
1.23
0.90
0.88
0.87
0.86
0.84
0.83
0.00
•HPF6
i-Pr2N nBu
N
N
P
N
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
i-Pr2N
Ni-Pr2
12•HPF6 (impure)
1H NMR (CDCl3, 500 MHz)
3.37
12.00
1.94
1.00
0.27
0.16
2.14
101.63
2.02
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

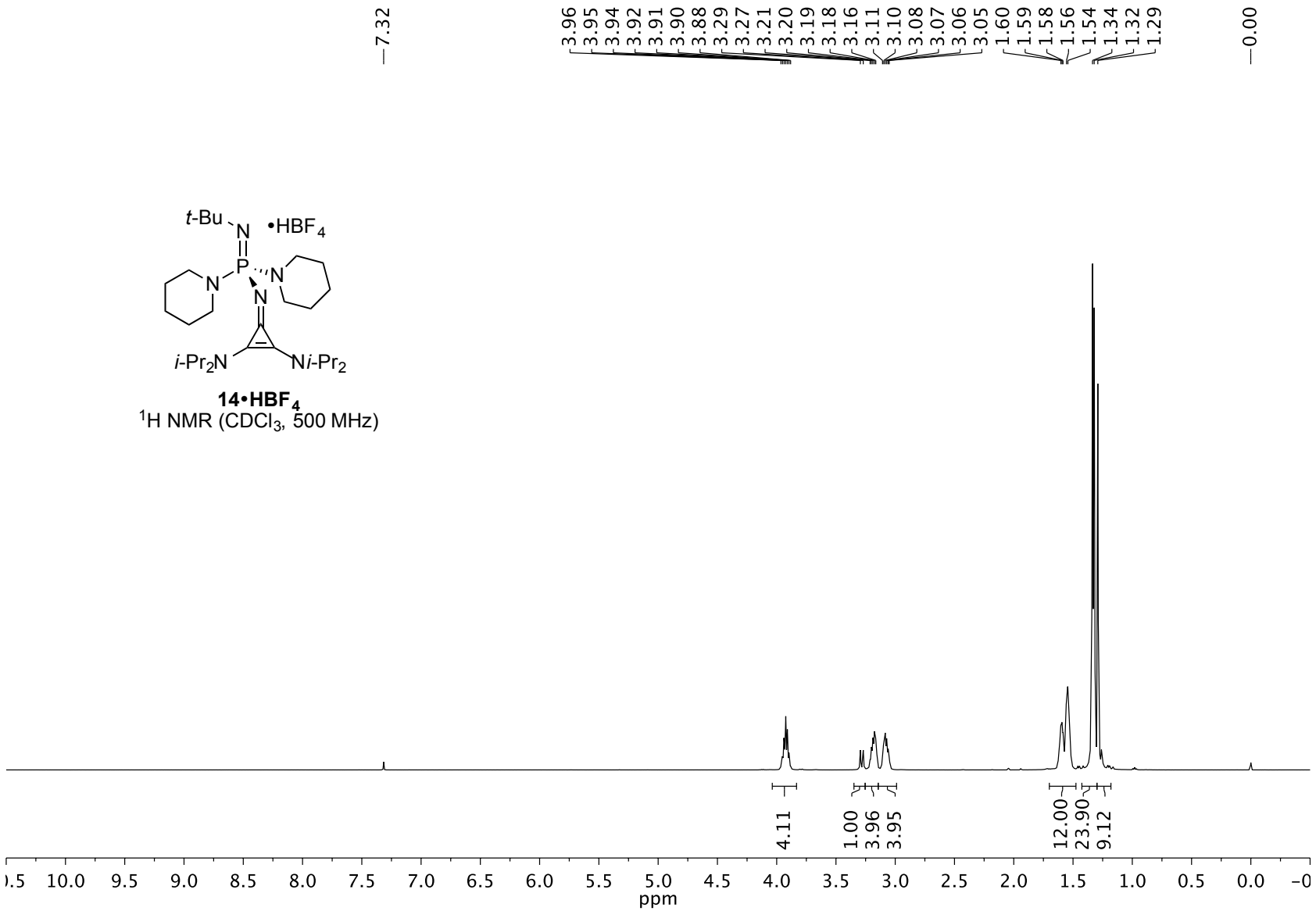


12•HPF$_6$ (impure)
^{13}C NMR ($CDCl_3$, 126 MHz)

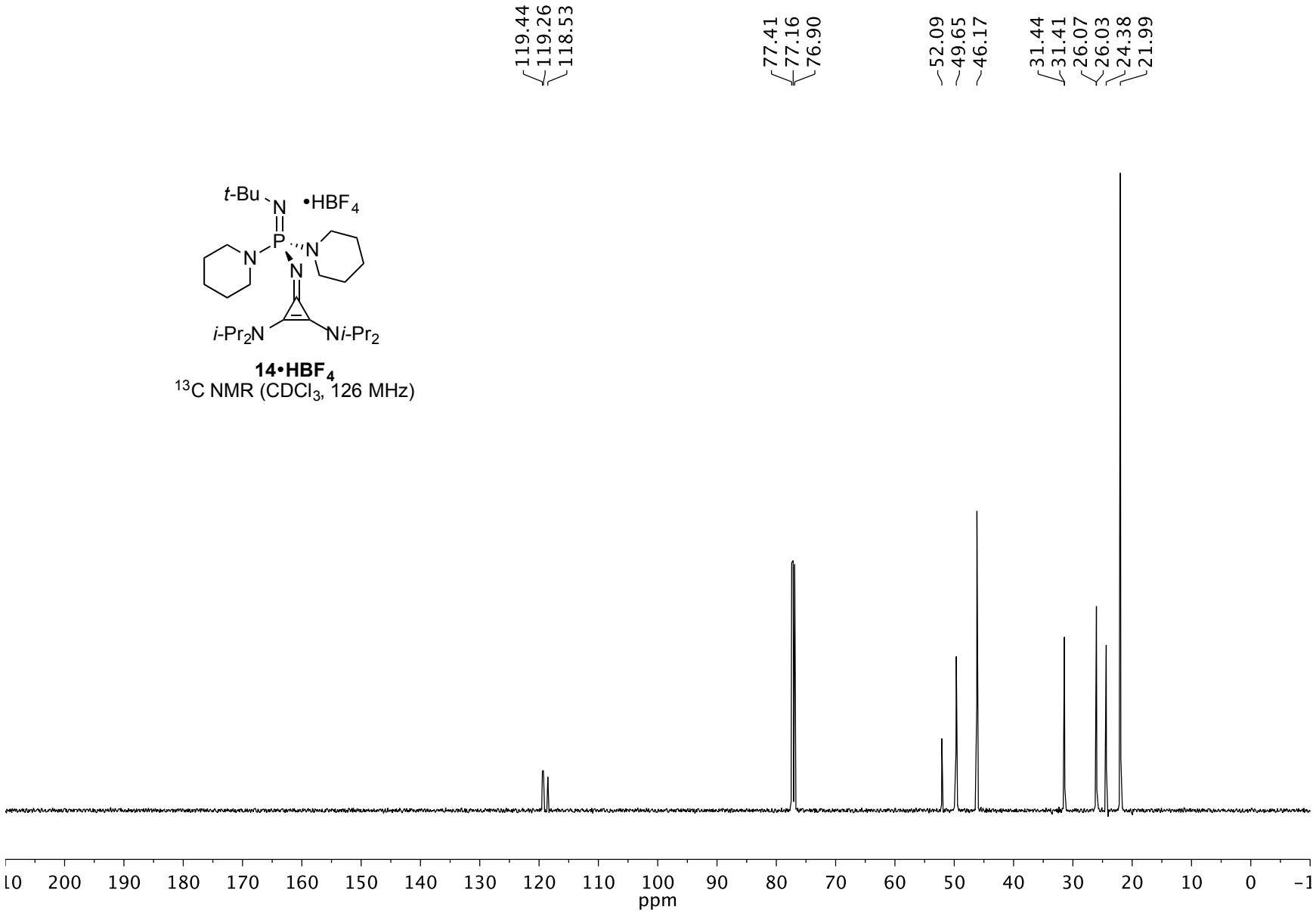
122.98
118.96
118.78
77.41
77.16
76.90
49.62
49.34
41.35
41.18
34.55
22.21
22.03
21.13
20.27
20.06
14.29
13.99

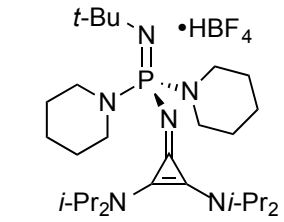


12•HPF$_6$ (impure)
^{31}P NMR ($CDCl_3$, 202 MHz)

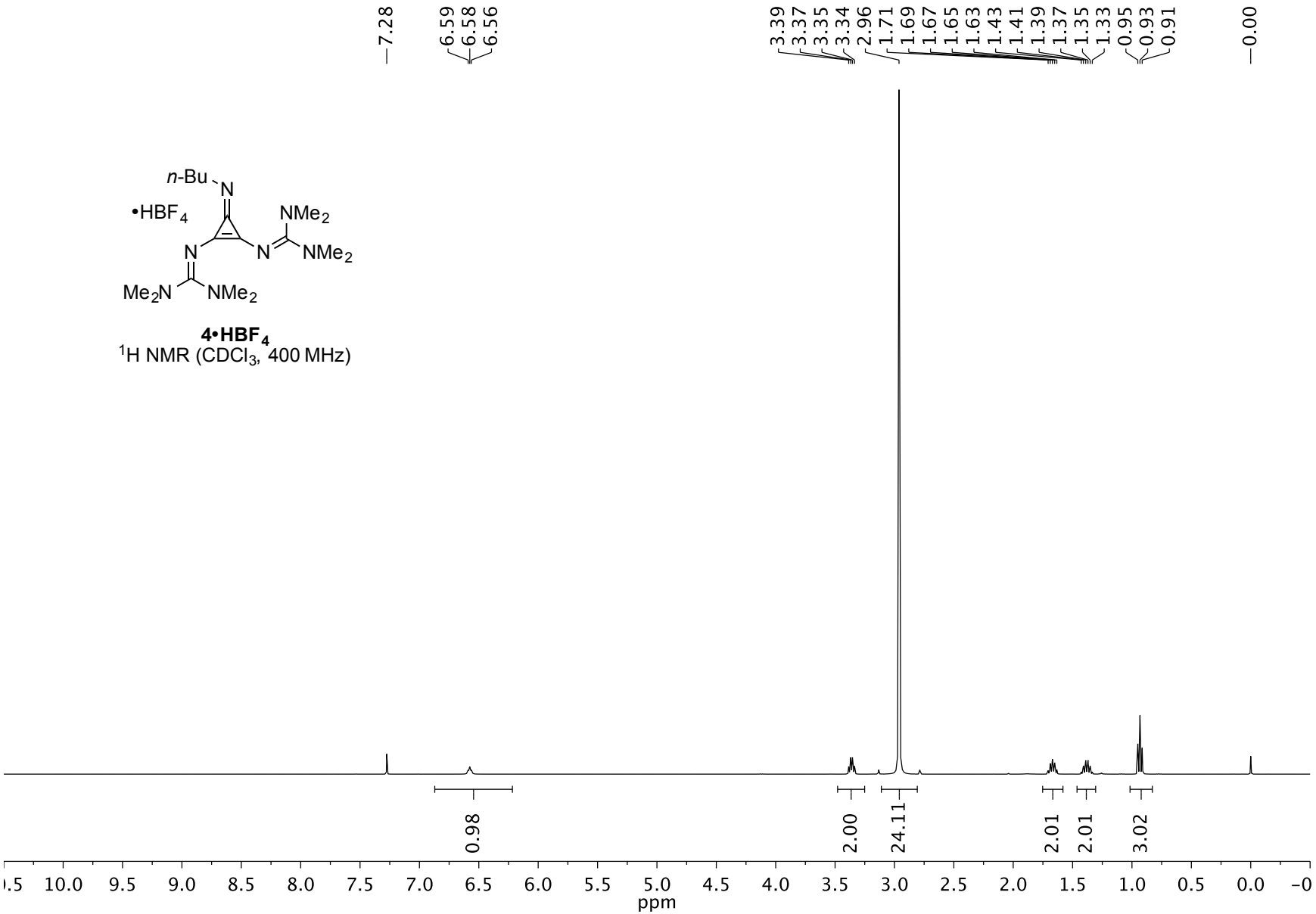


14•HBF$_4$
^{1}H NMR ($CDCl_3$, 500 MHz)

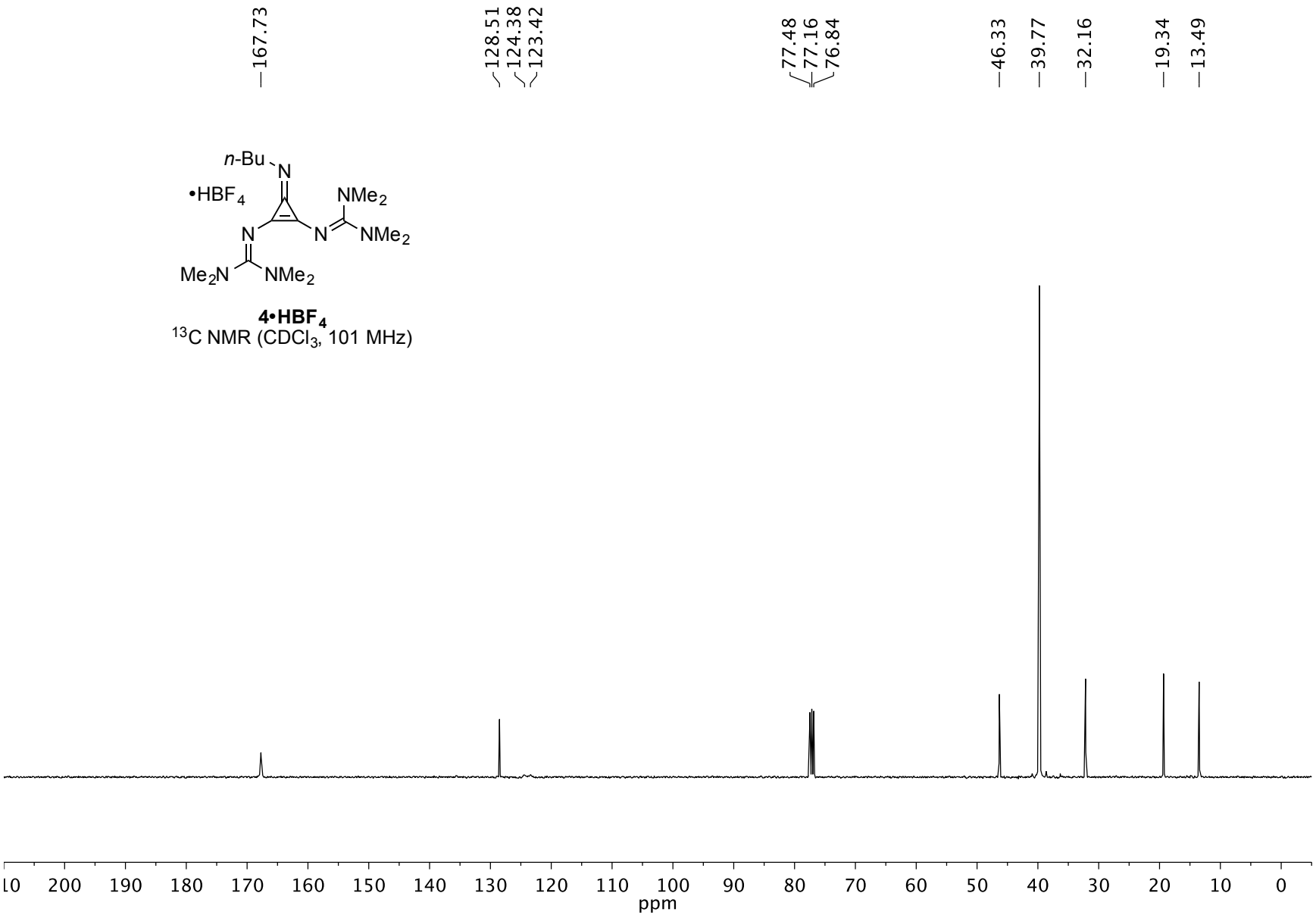

119.44
119.26
118.53
77.41
77.16
76.90
52.09
49.65
46.17
31.44
31.41
26.07
26.03
24.38
21.99
t-Bu
N
•HBF4
P
N
N
N
i-Pr2N
Ni-Pr2
14•HBF4
13C NMR (CDCl3, 126 MHz)
ppm



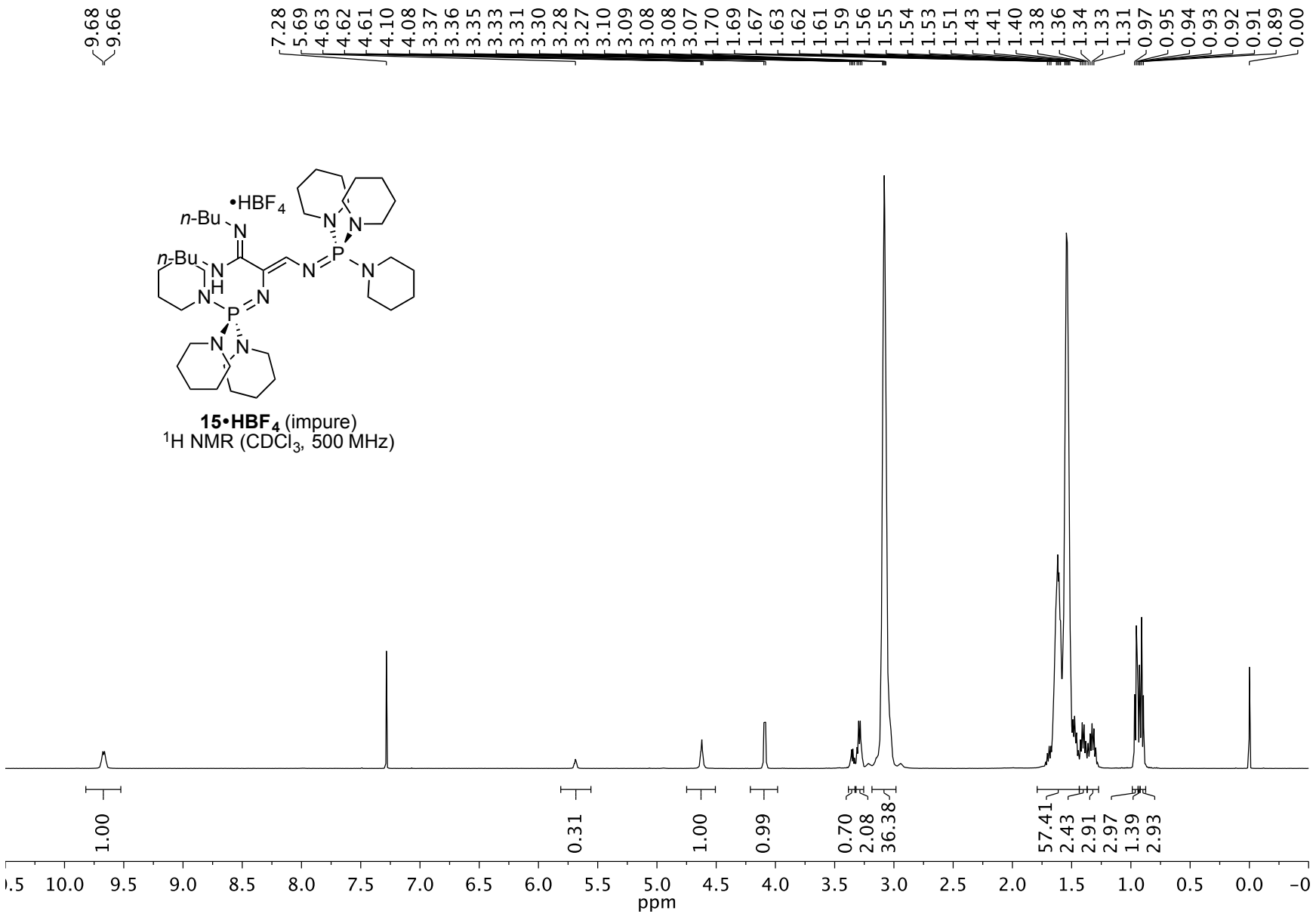
14•HBF$_4$
^{31}P NMR ($CDCl_3$, 121 MHz)



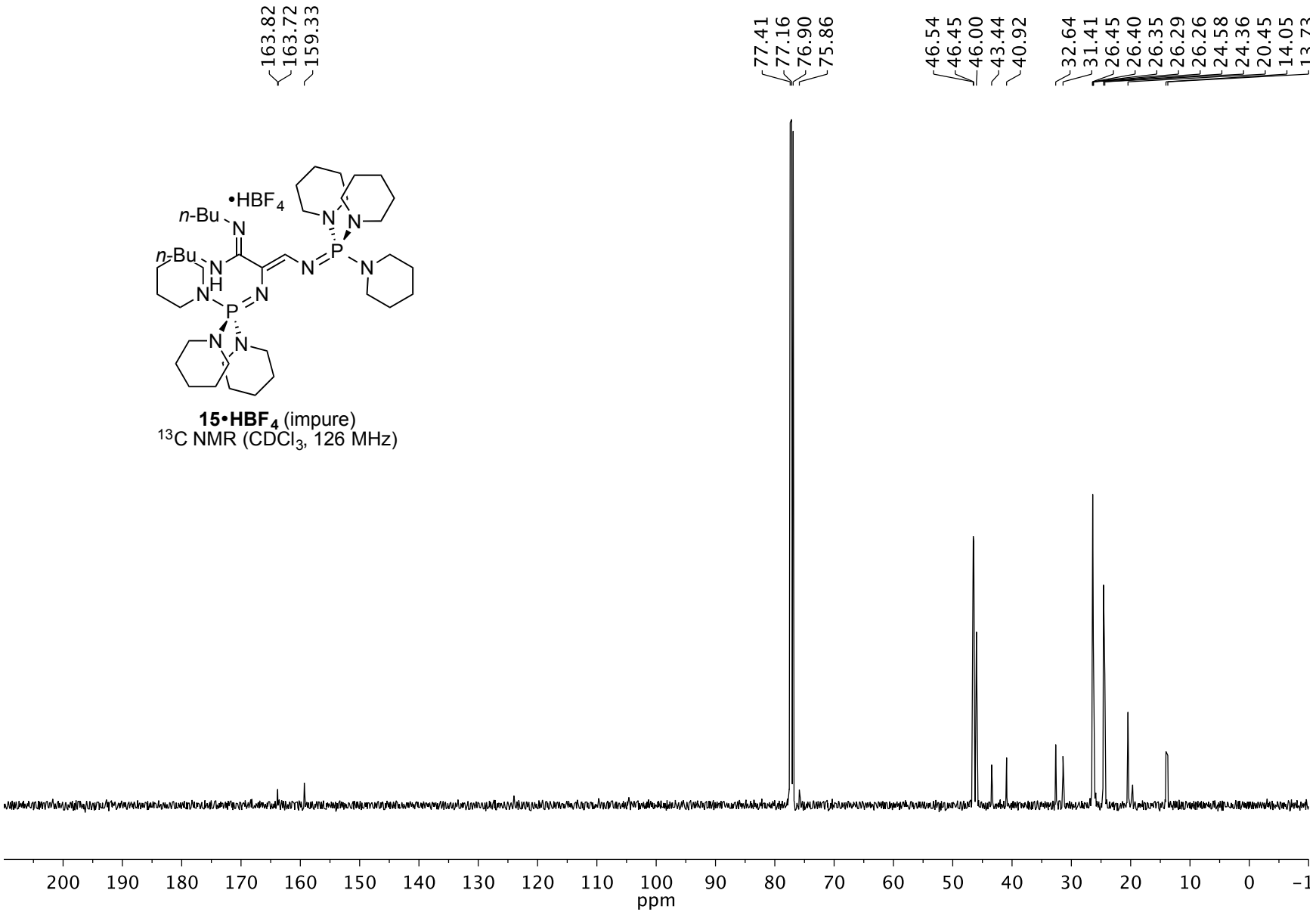
4•HBF$_4$
^{1}H NMR ($CDCl_3$, 400 MHz)



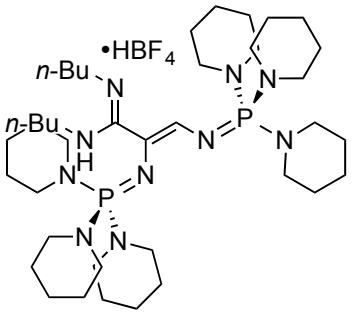
4•HBF$_4$
^{13}C NMR ($CDCl_3$, 101 MHz)



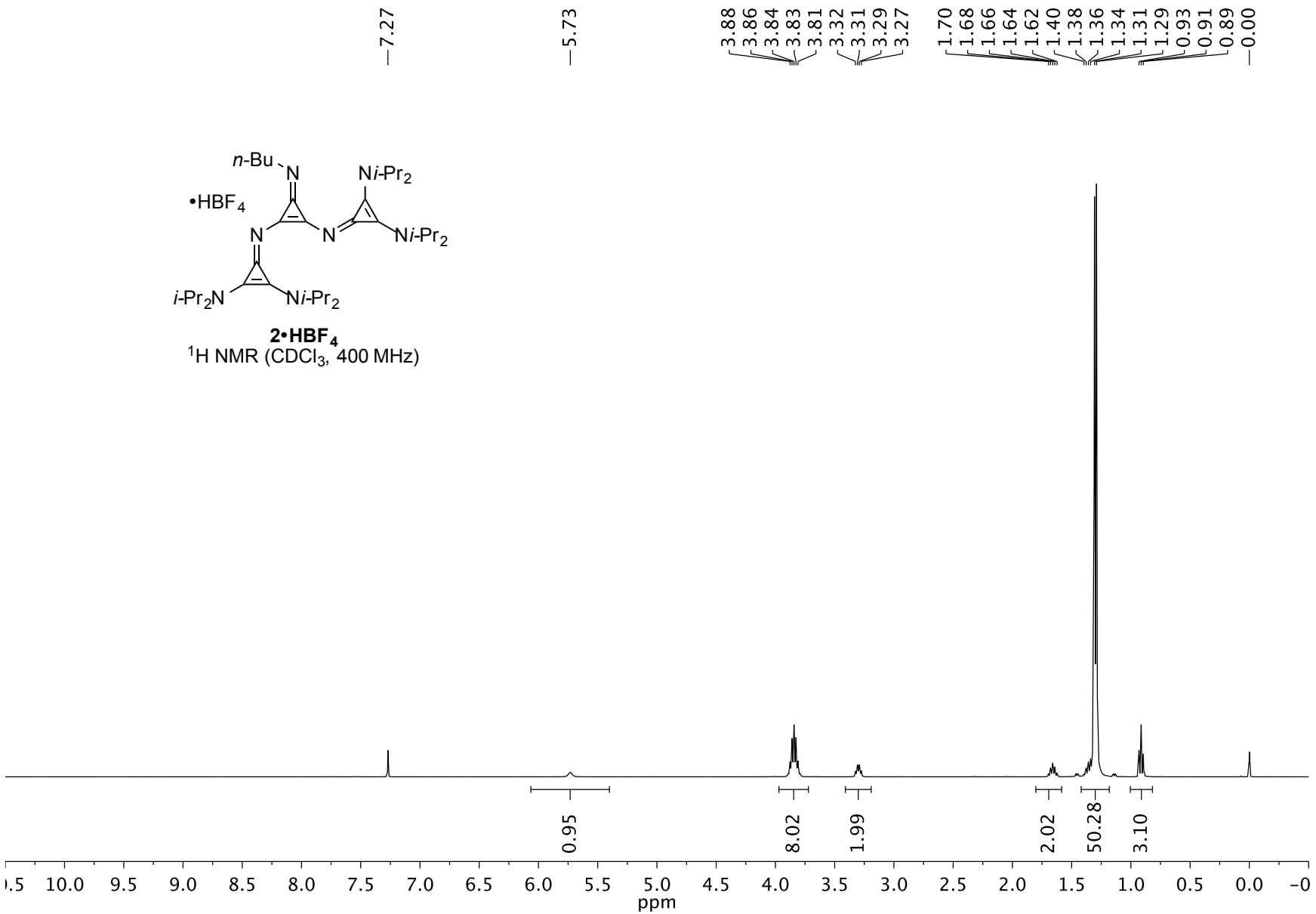
15•HBF$_4$ (impure)
^{1}H NMR ($CDCl_3$, 500 MHz)

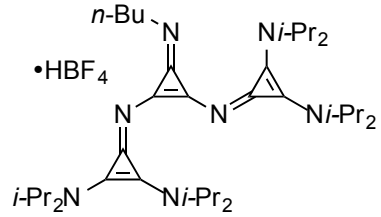


15•HBF$_4$ (impure)
^{13}C NMR ($CDCl_3$, 126 MHz)



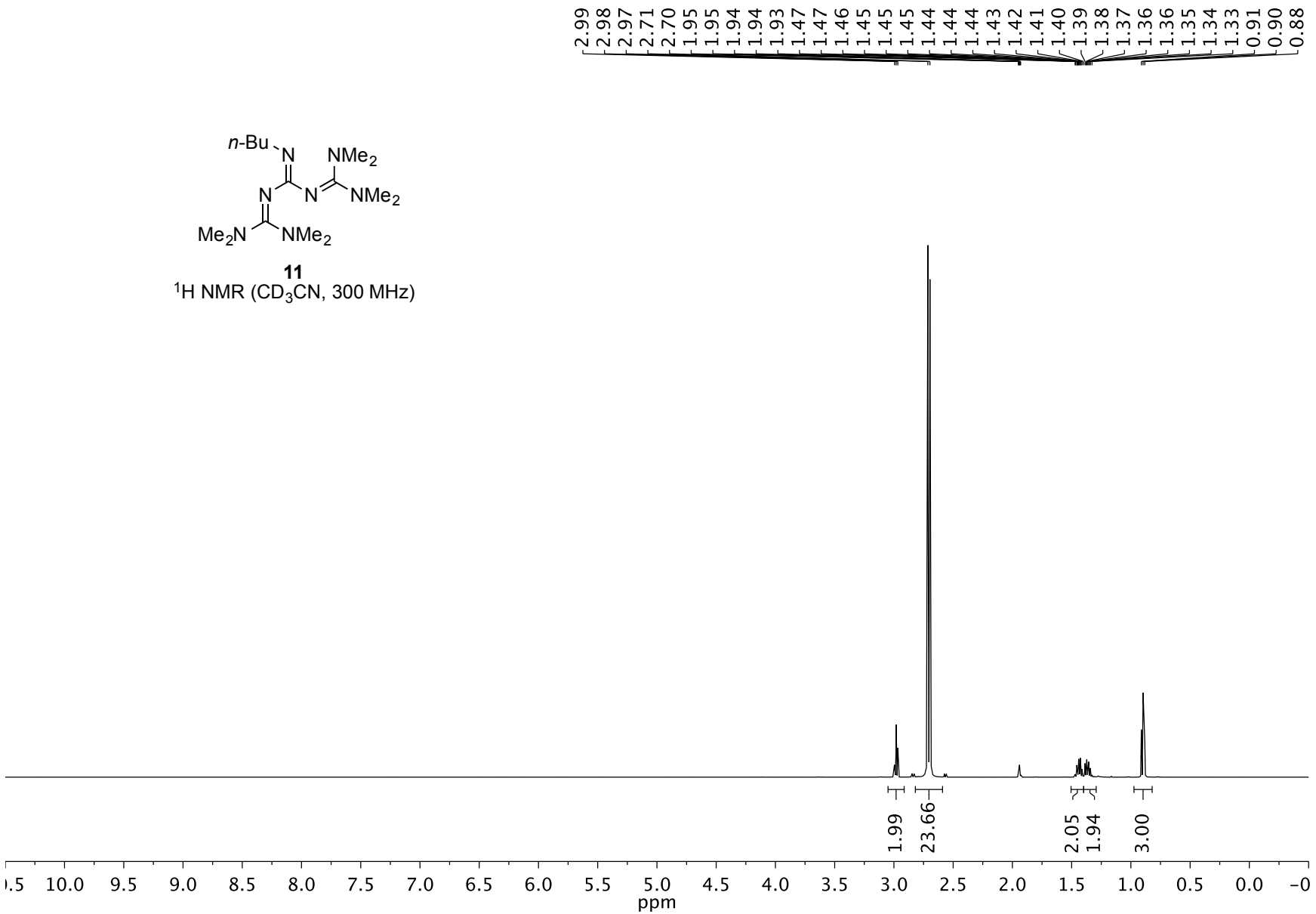
15•HBF$_4$ (impure)
^{31}P NMR ($CDCl_3$, 202 MHz)

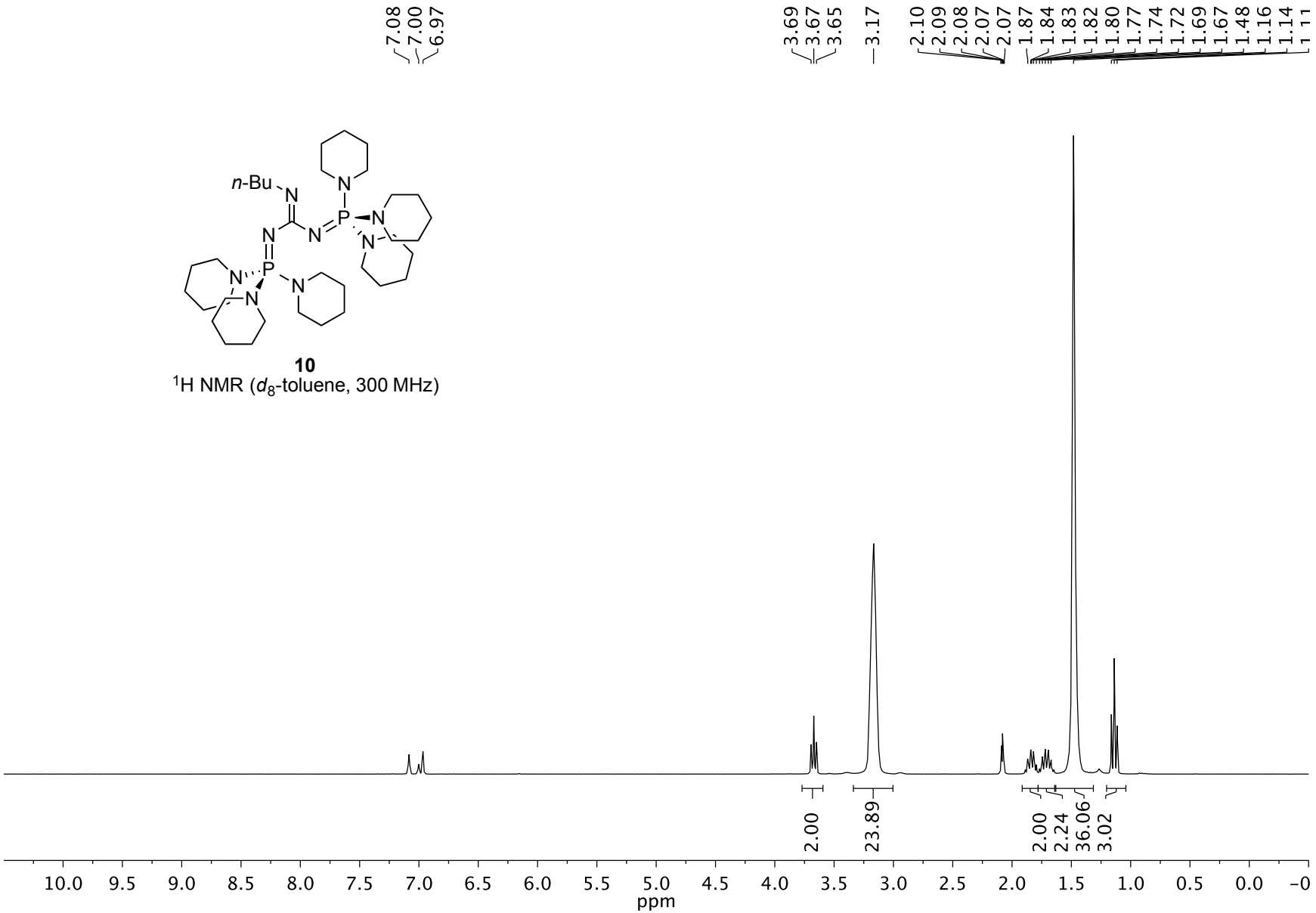

7.27
5.73
3.88
3.86
3.84
3.83
3.81
3.32
3.31
3.29
3.27
1.70
1.68
1.66
1.64
1.62
1.40
1.38
1.36
1.34
1.31
1.29
0.93
0.91
0.89
0.00
n-Bu
N
Ni-Pr2
•HBF4
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
2•HBF4
1H NMR (CDCl3, 400 MHz)
0.95
8.02
1.99
2.02
50.28
3.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
ppm



2•HBF$_4$

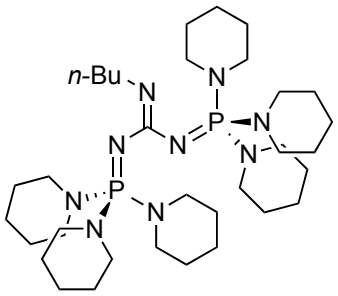
^{13}C NMR ($CDCl_3$, 101 MHz)


2.99
2.98
2.97
2.71
2.70
1.95
1.95
1.94
1.94
1.93
1.47
1.47
1.46
1.45
1.45
1.45
1.44
1.44
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.36
1.36
1.35
1.34
1.33
0.91
0.90
0.88
n-Bu
N
NMe2
N
N
NMe2
Me2N
NMe2
11
1H NMR (CD3CN, 300 MHz)
1.99
23.66
2.05
1.94
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



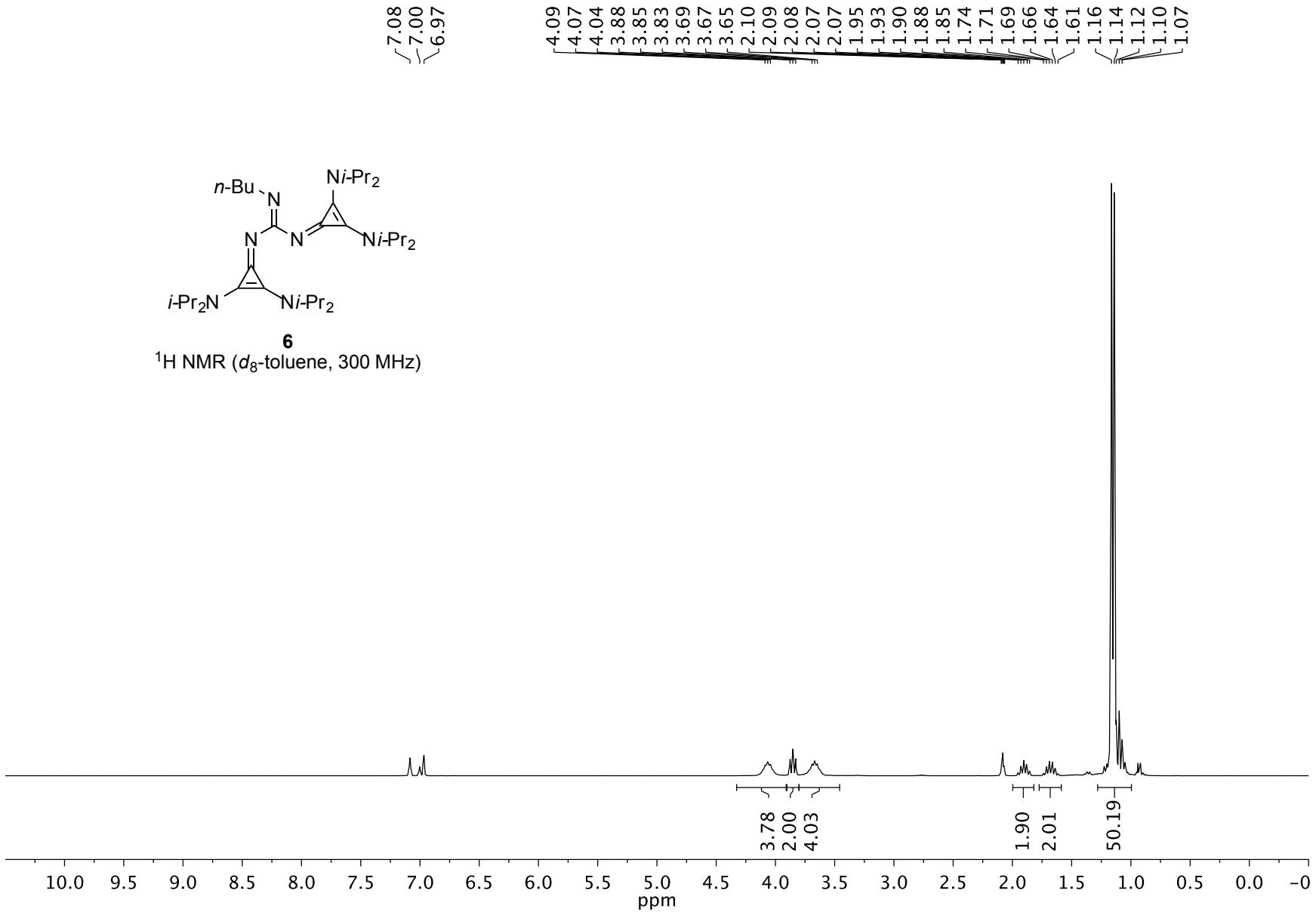
10

^{1}H NMR (d_8-toluene, 300 MHz)



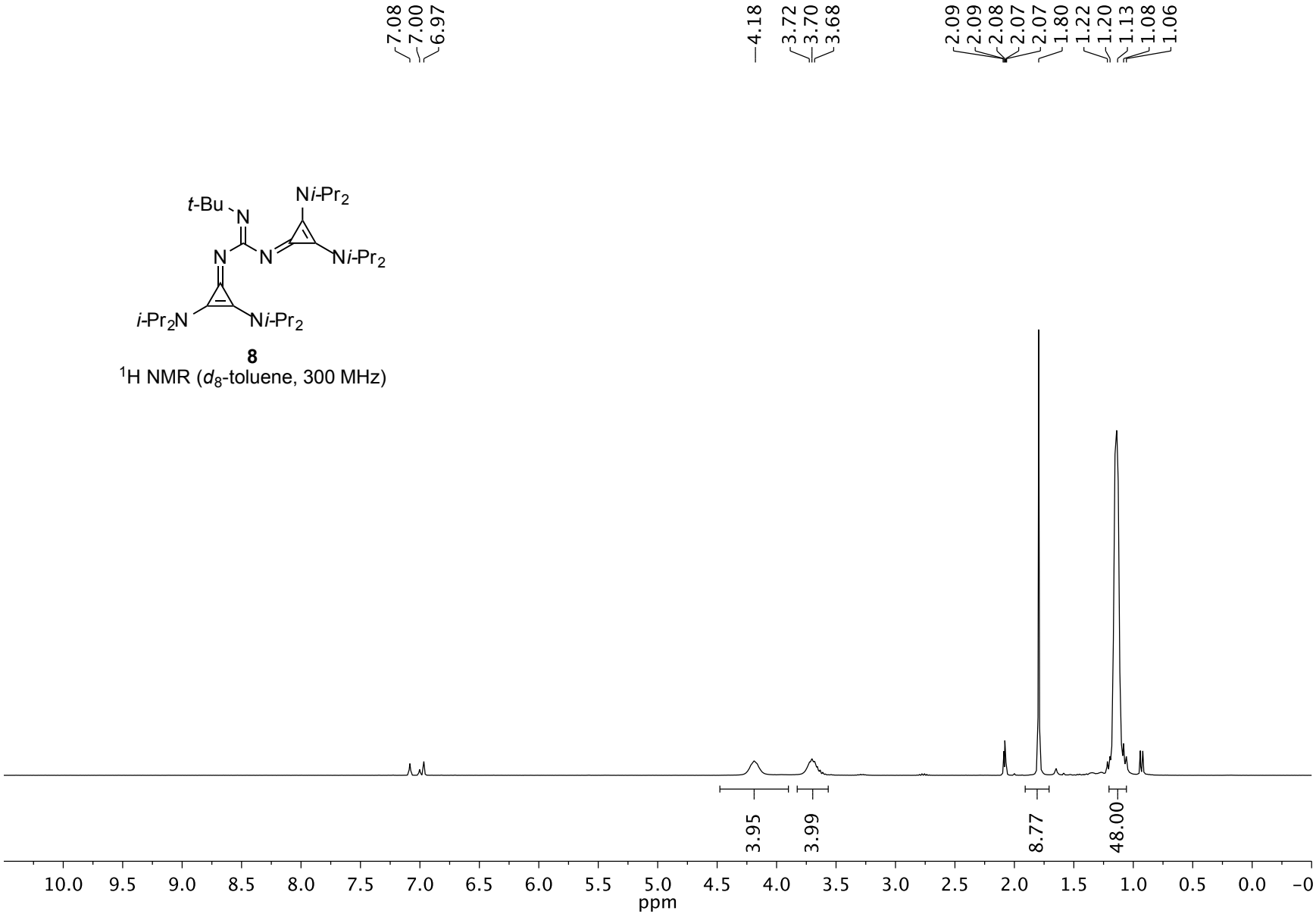
10

^{31}P NMR (d_8-toluene, 121 MHz)



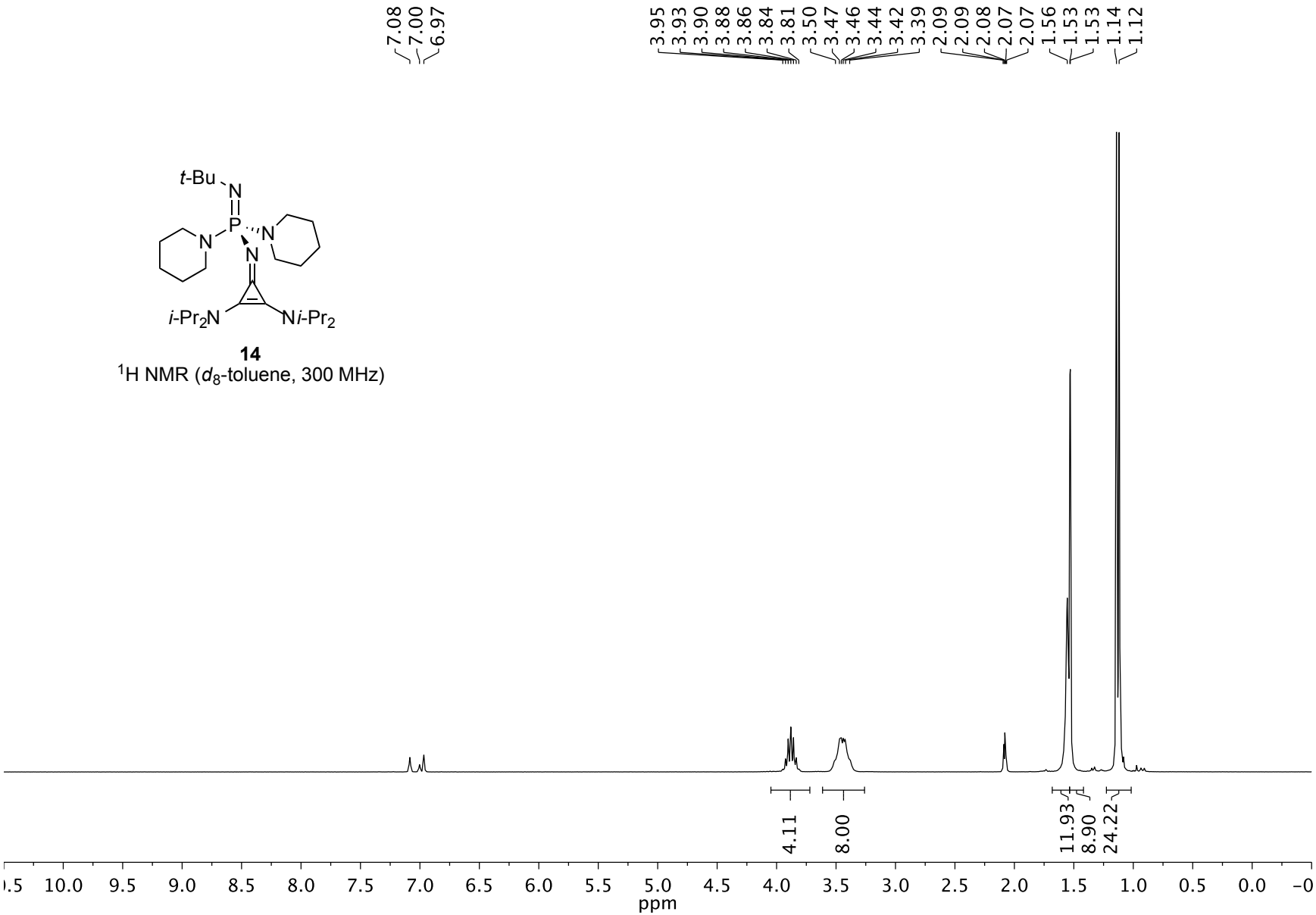
6

^{1}H NMR (d_8-toluene, 300 MHz)



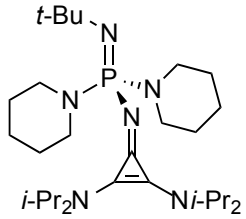
8

^{1}H NMR (d_8-toluene, 300 MHz)



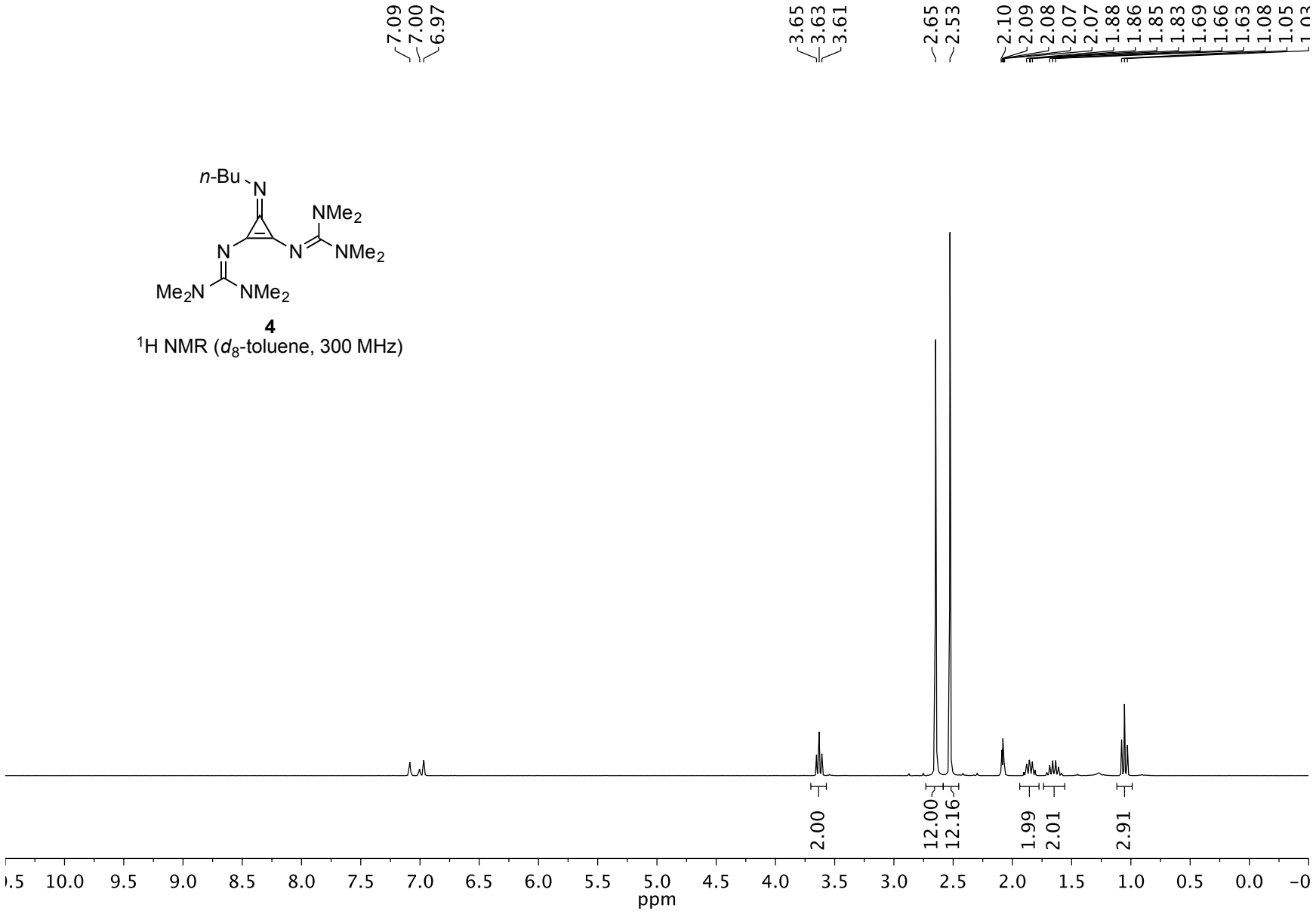
14

^{1}H NMR (d_8-toluene, 300 MHz)



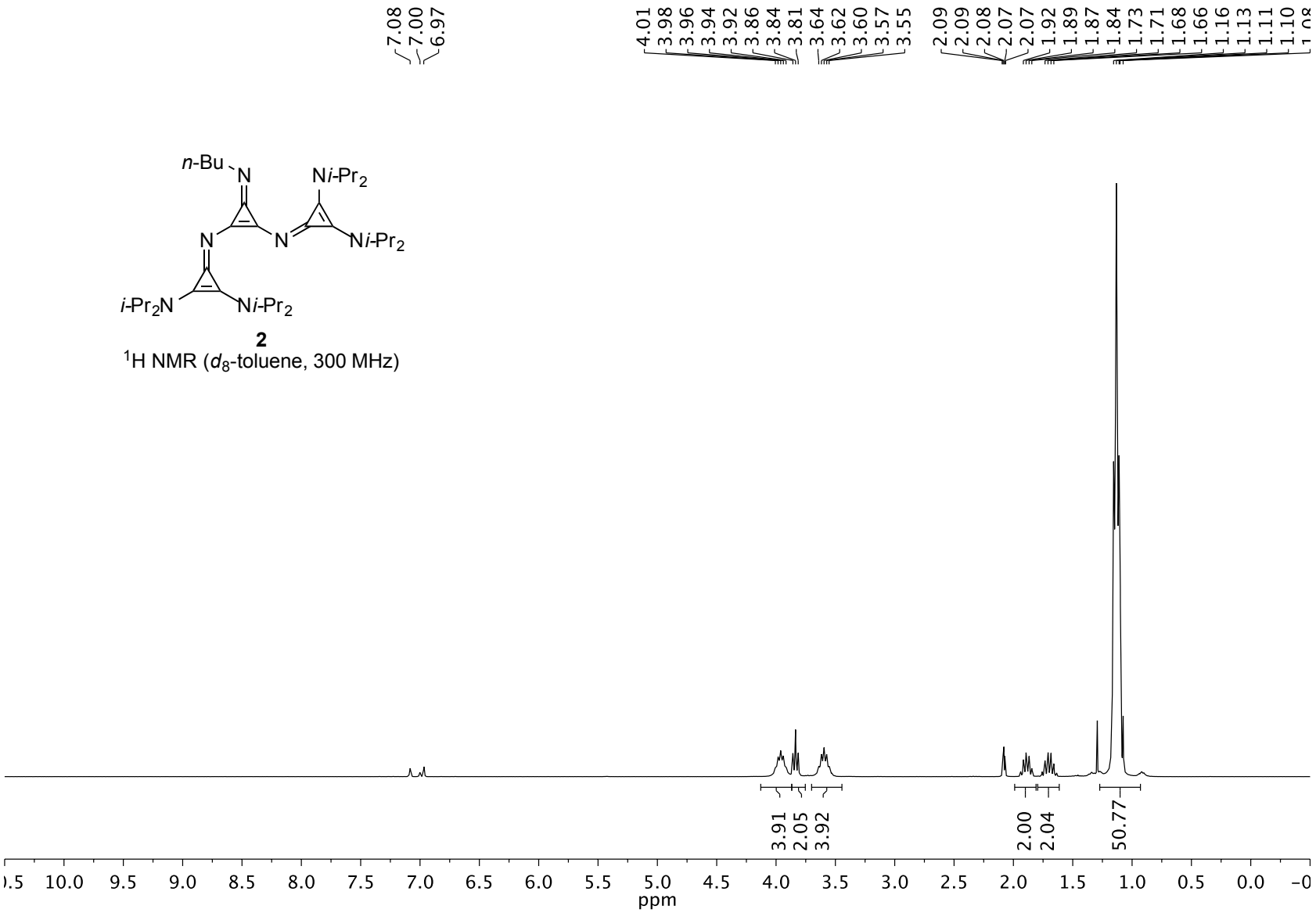
14

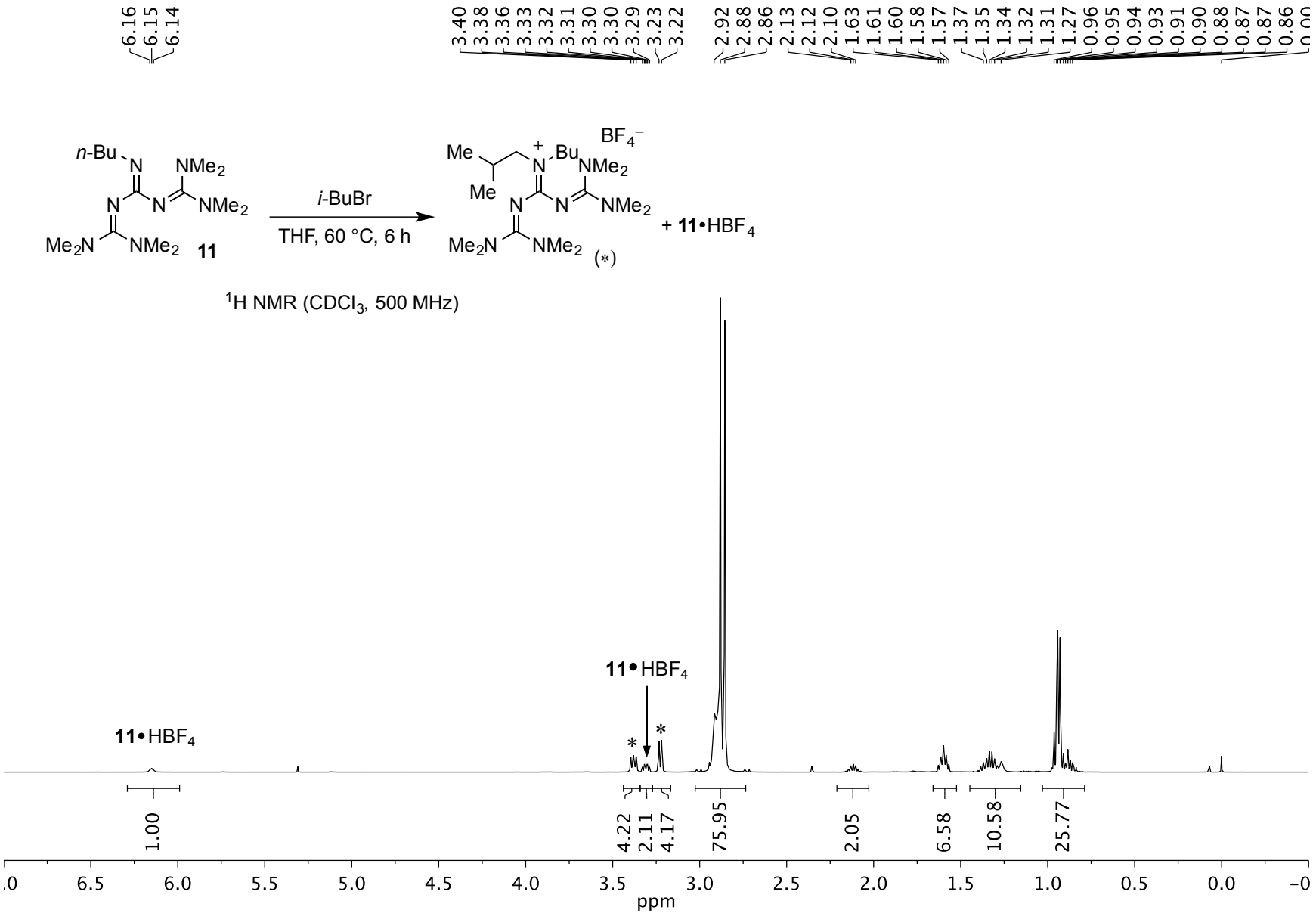
^{31}P NMR (d_8-toluene, 121 MHz)

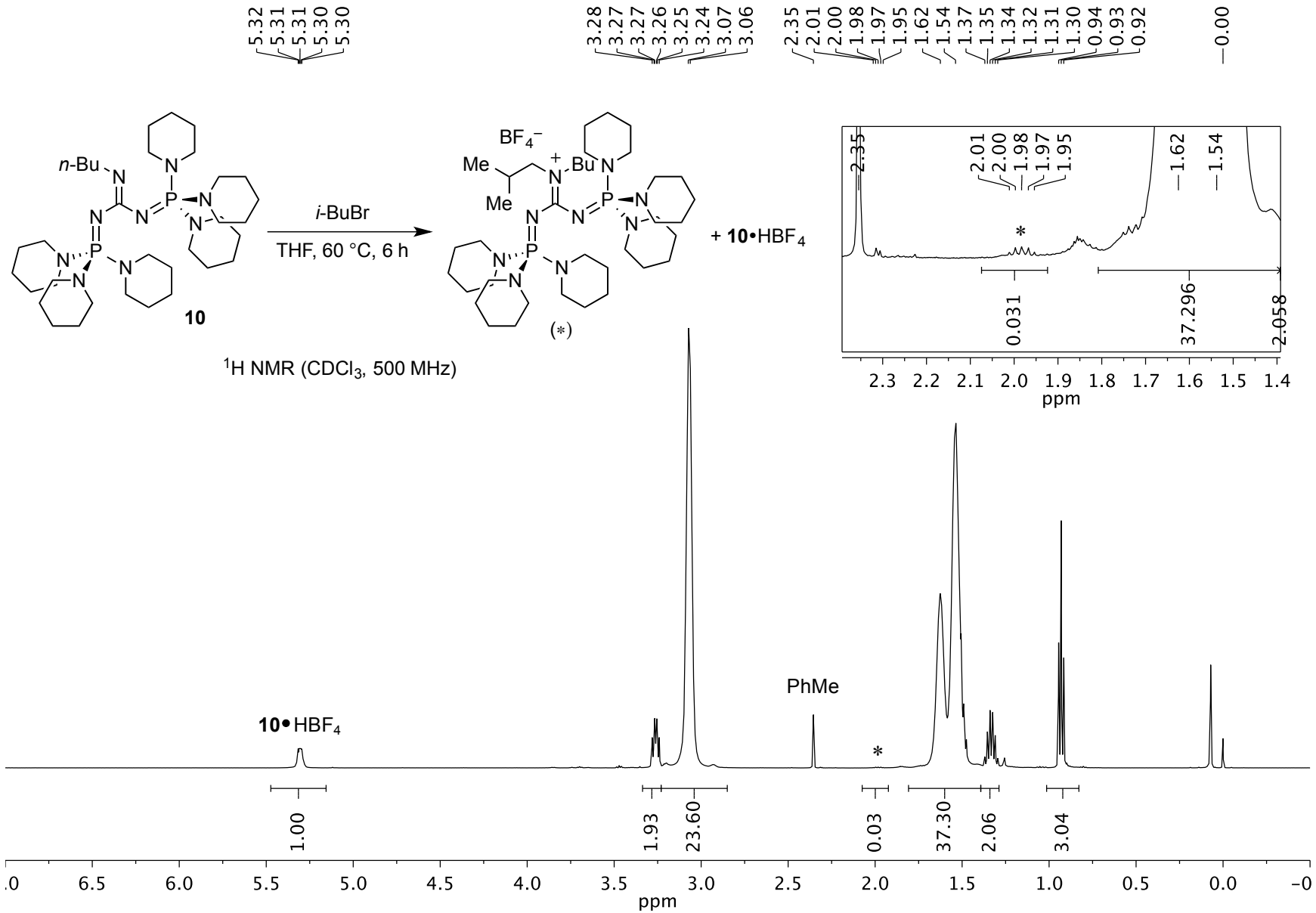


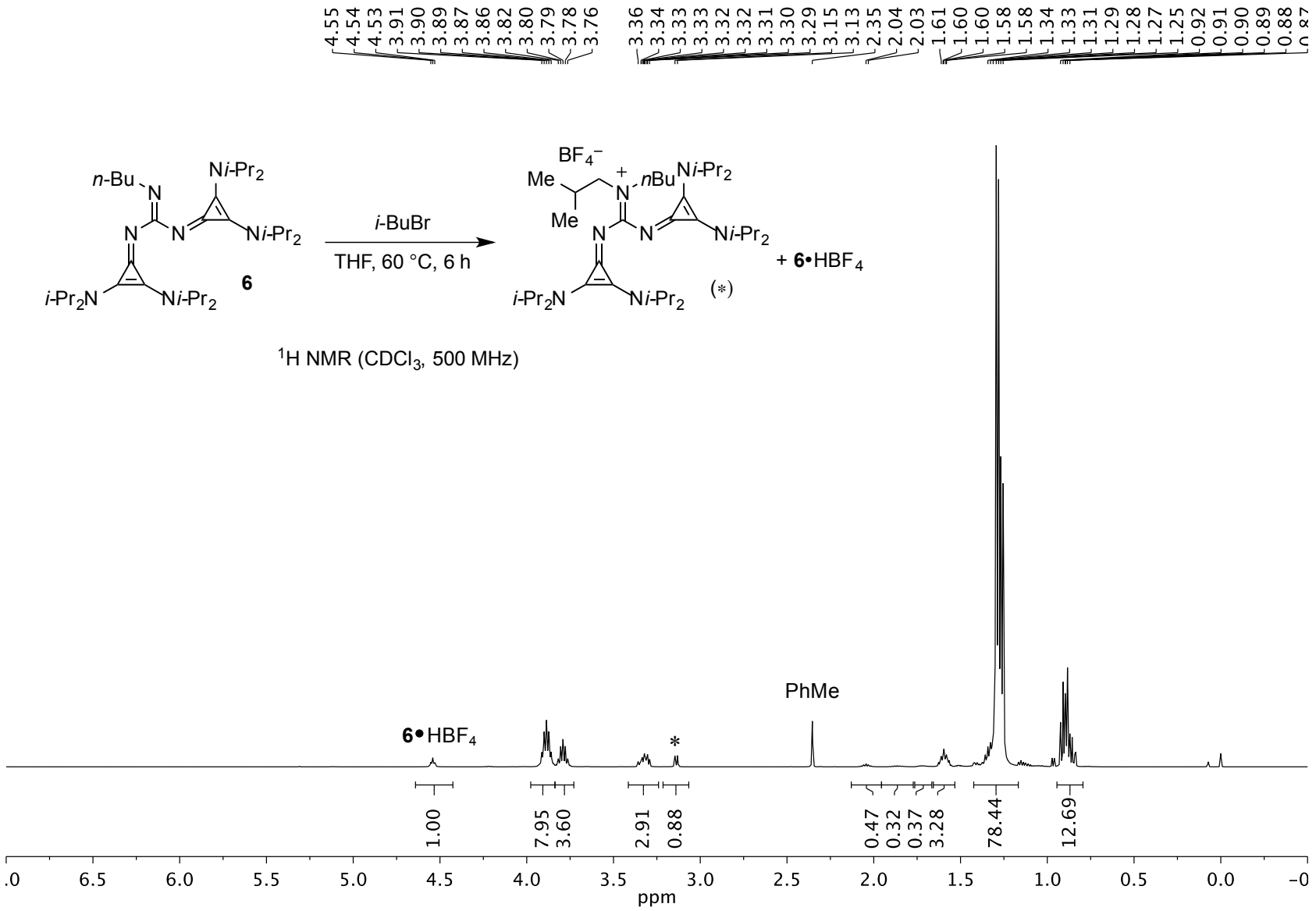
4

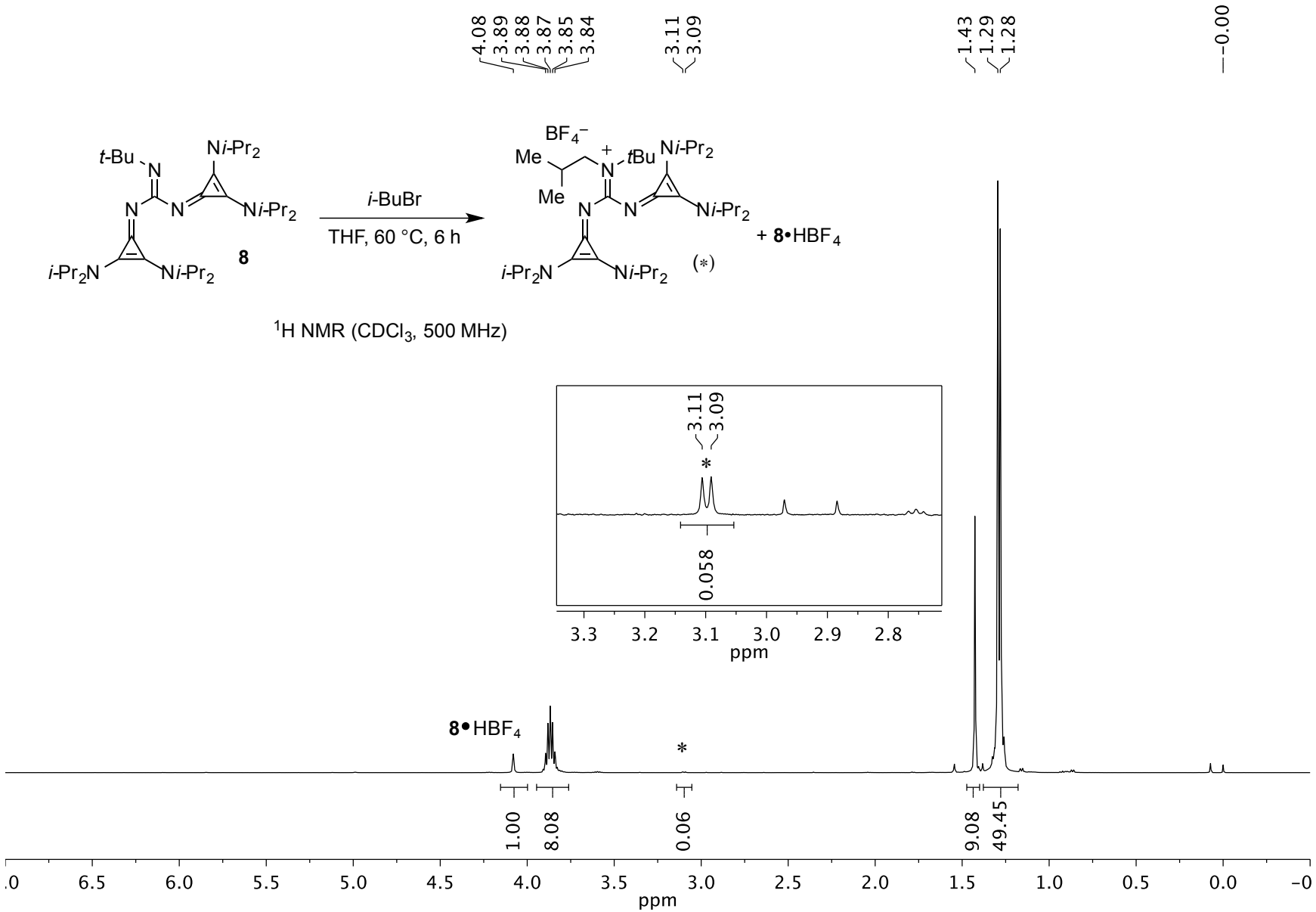
^{1}H NMR (d_8-toluene, 300 MHz)

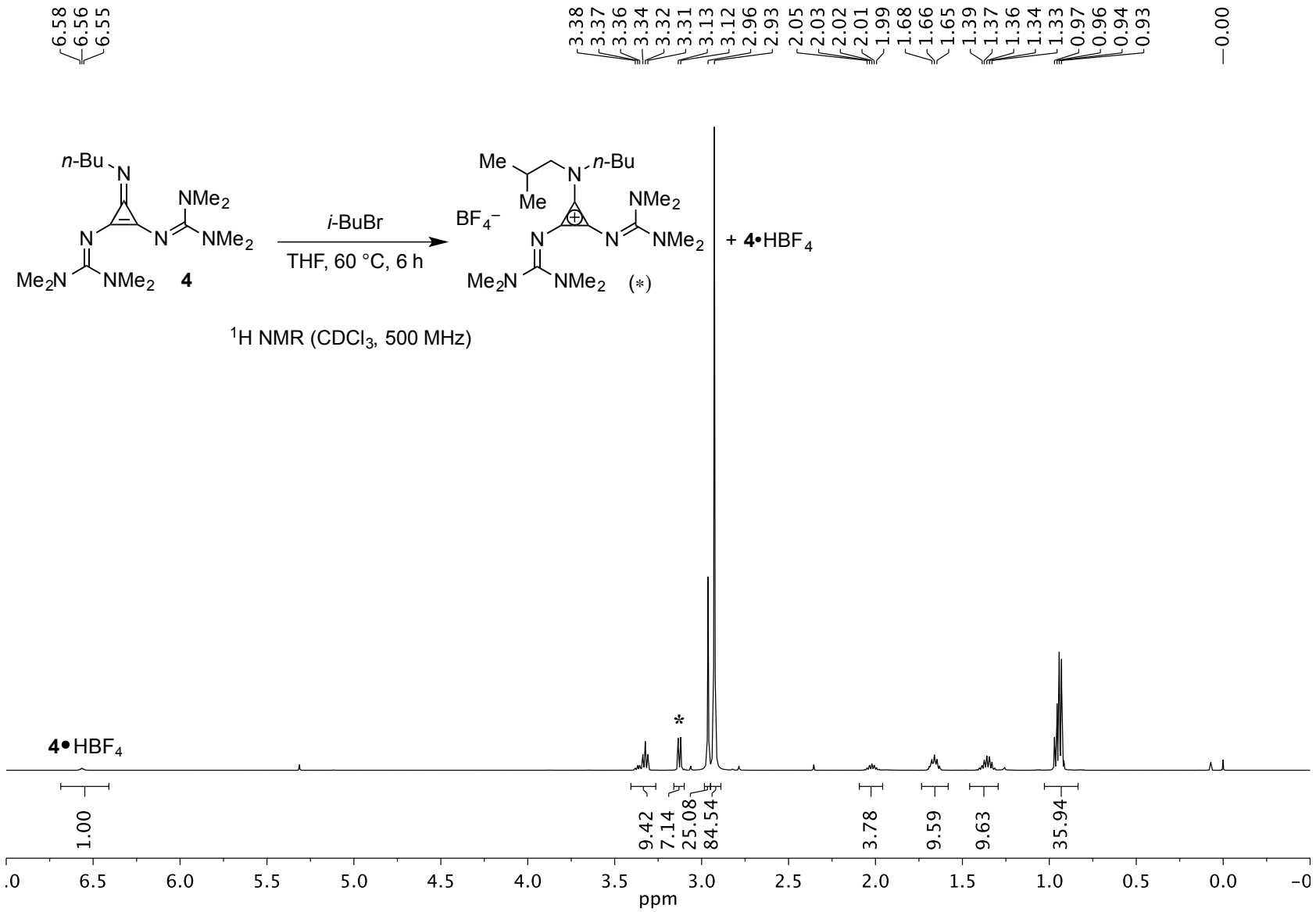

7.08
7.00
6.97
4.01
3.98
3.96
3.94
3.92
3.86
3.84
3.81
3.64
3.62
3.60
3.57
3.55
2.09
2.09
2.08
2.07
2.07
1.92
1.89
1.87
1.84
1.73
1.71
1.68
1.66
1.16
1.13
1.11
1.10
n-Bu
N
Ni-Pr2
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
2
1H NMR (d8-toluene, 300 MHz)
3.91
2.05
3.92
2.00
2.04
50.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

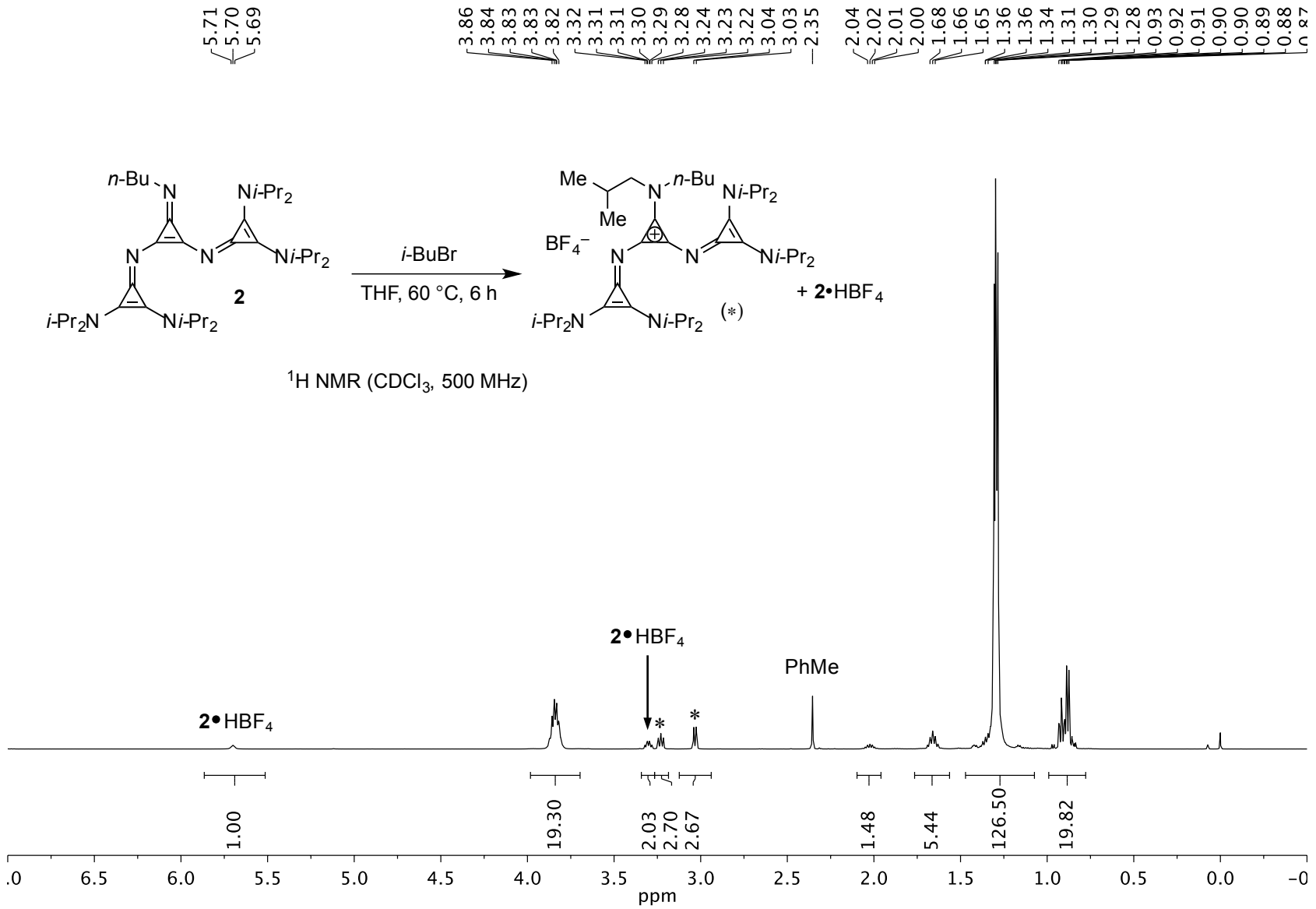

6.16
6.15
6.14
3.40
3.38
3.36
3.33
3.32
3.31
3.30
3.30
3.29
3.23
3.22
2.92
2.88
2.86
2.13
2.12
2.10
1.63
1.61
1.60
1.58
1.57
1.37
1.35
1.34
1.32
1.31
1.27
0.96
0.95
0.94
0.93
0.91
0.90
0.88
0.87
0.87
0.86
n-Bu
NMe2
Me2N
11
i-BuBr
THF, 60 °C, 6 h
Me
Bu
BF4−
(*)
+ 11•HBF4
1H NMR (CDCl3, 500 MHz)
11•HBF4
11•HBF4
1.00
4.22
2.11
4.17
75.95
2.05
6.58
10.58
25.77
ppm

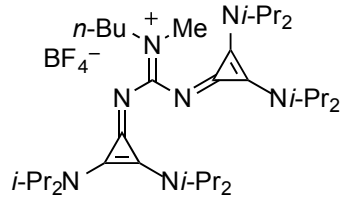

5.32
5.31
5.31
5.30
5.30
3.28
3.27
3.27
3.26
3.25
3.24
3.07
3.06
2.35
2.01
2.00
1.98
1.97
1.95
1.62
1.54
1.37
1.35
1.34
1.32
1.31
1.30
0.94
0.93
0.92
0.00
n-Bu
i-BuBr
THF, 60 °C, 6 h
10
BF4−
Me
Me
Bu
(*)
+ 10•HBF4
1H NMR (CDCl3, 500 MHz)
2.35
2.01
2.00
1.98
1.97
1.95
1.62
1.54
0.031
37.296
2.058
ppm
10•HBF4
PhMe
1.00
1.93
23.60
0.03
37.30
2.06
3.04
ppm


4.55 4.54 4.53 3.91 3.90 3.89 3.87 3.86 3.82 3.80 3.79 3.78 3.76
3.36 3.34 3.33 3.33 3.32 3.32 3.31 3.30 3.29 3.15 3.13 2.35 2.04 2.03
1.61 1.60 1.60 1.58 1.58 1.34 1.33 1.31 1.29 1.28 1.27 1.25 0.92 0.91 0.90 0.89 0.88
n-Bu
Ni-Pr2
N
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
6
i-BuBr
THF, 60 °C, 6 h
BF4−
Me
Me
+
N
nBu
Ni-Pr2
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
(*)
+ 6•HBF4
1H NMR (CDCl3, 500 MHz)
PhMe
6•HBF4
*
1.00
7.95
3.60
2.91
0.88
0.47
0.32
0.37
3.28
78.44
12.69
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


4.08
3.89
3.88
3.87
3.85
3.84
3.11
3.09
1.43
1.29
1.28
0.00
t-Bu
N
N
N
N
Ni-Pr2
Ni-Pr2
i-Pr2N
Ni-Pr2
8
i-BuBr
THF, 60 °C, 6 h
BF4−
Me
Me
+
N
tBu
Ni-Pr2
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
(*)
+ 8•HBF4
1H NMR (CDCl3, 500 MHz)
3.11
3.09
*
0.058
3.3
3.2
3.1
3.0
2.9
2.8
ppm
8•HBF4
*
1.00
8.08
0.06
9.08
49.45
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

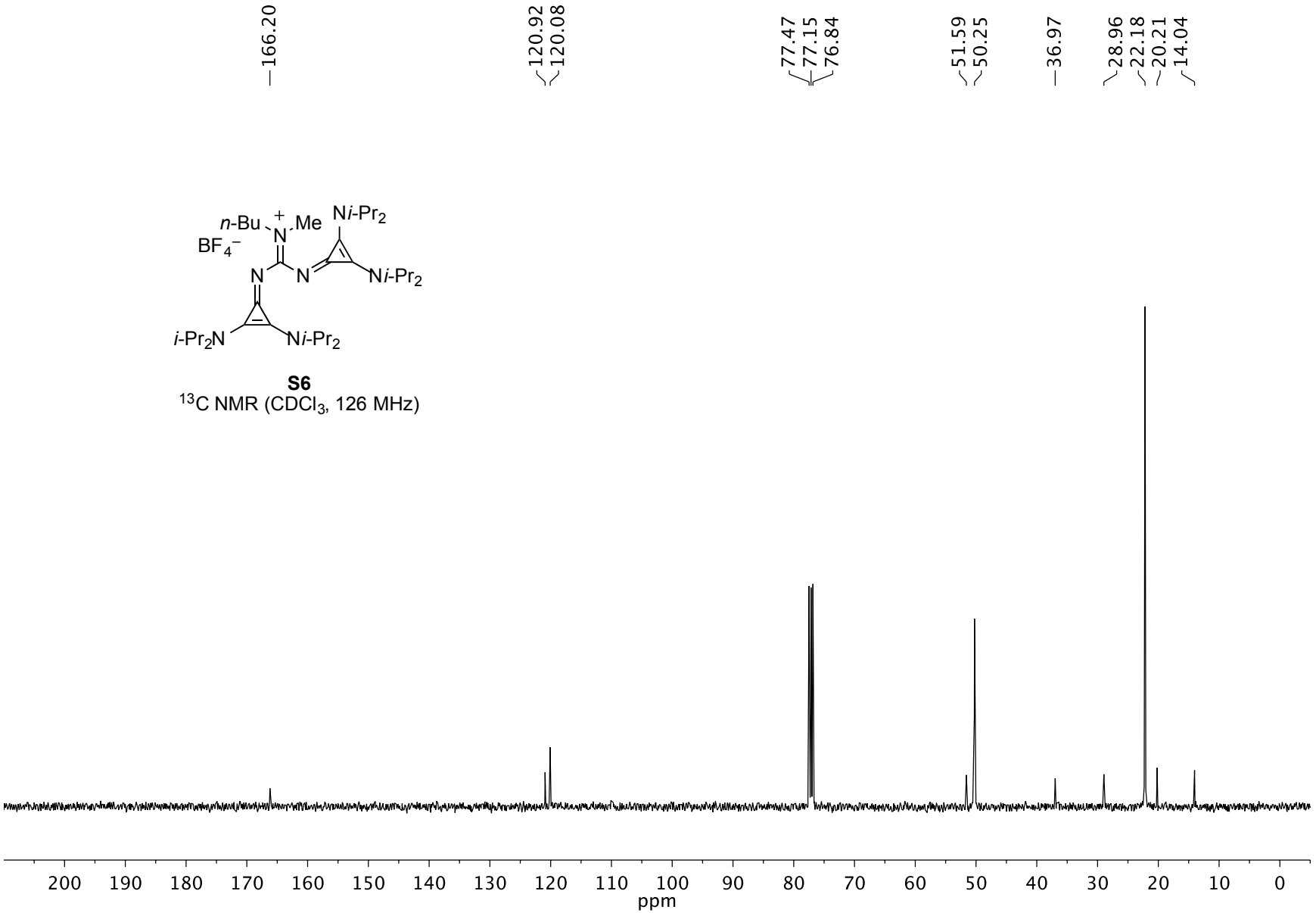

6.58
6.56
6.55
3.38
3.37
3.36
3.34
3.32
3.31
3.13
3.12
2.96
2.93
2.05
2.03
2.02
2.01
1.99
1.68
1.66
1.65
1.39
1.37
1.36
1.34
1.33
0.97
0.96
0.94
0.93
0.00
n-Bu
NMe2
Me2N
NMe2
4
i-BuBr
THF, 60 °C, 6 h
Me
n-Bu
BF4−
(*)
+ 4•HBF4
1H NMR (CDCl3, 500 MHz)
4•HBF4
*
1.00
9.42
7.14
25.08
84.54
3.78
9.59
9.63
35.94
ppm


5.71
5.70
5.69
3.86
3.84
3.83
3.83
3.82
3.32
3.31
3.31
3.30
3.29
3.28
3.24
3.23
3.22
3.04
3.03
2.35
2.04
2.02
2.01
2.00
1.68
1.66
1.65
1.36
1.36
1.34
1.31
1.30
1.29
1.28
0.93
0.92
0.91
0.90
0.90
0.89
0.88
n-Bu
N
Ni-Pr2
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
2
i-BuBr
THF, 60 °C, 6 h
Me
Me
n-Bu
BF4−
+ 2•HBF4
(*)
1H NMR (CDCl3, 500 MHz)
2•HBF4
PhMe
1.00
19.30
2.03
2.70
2.67
1.48
5.44
126.50
19.82
ppm



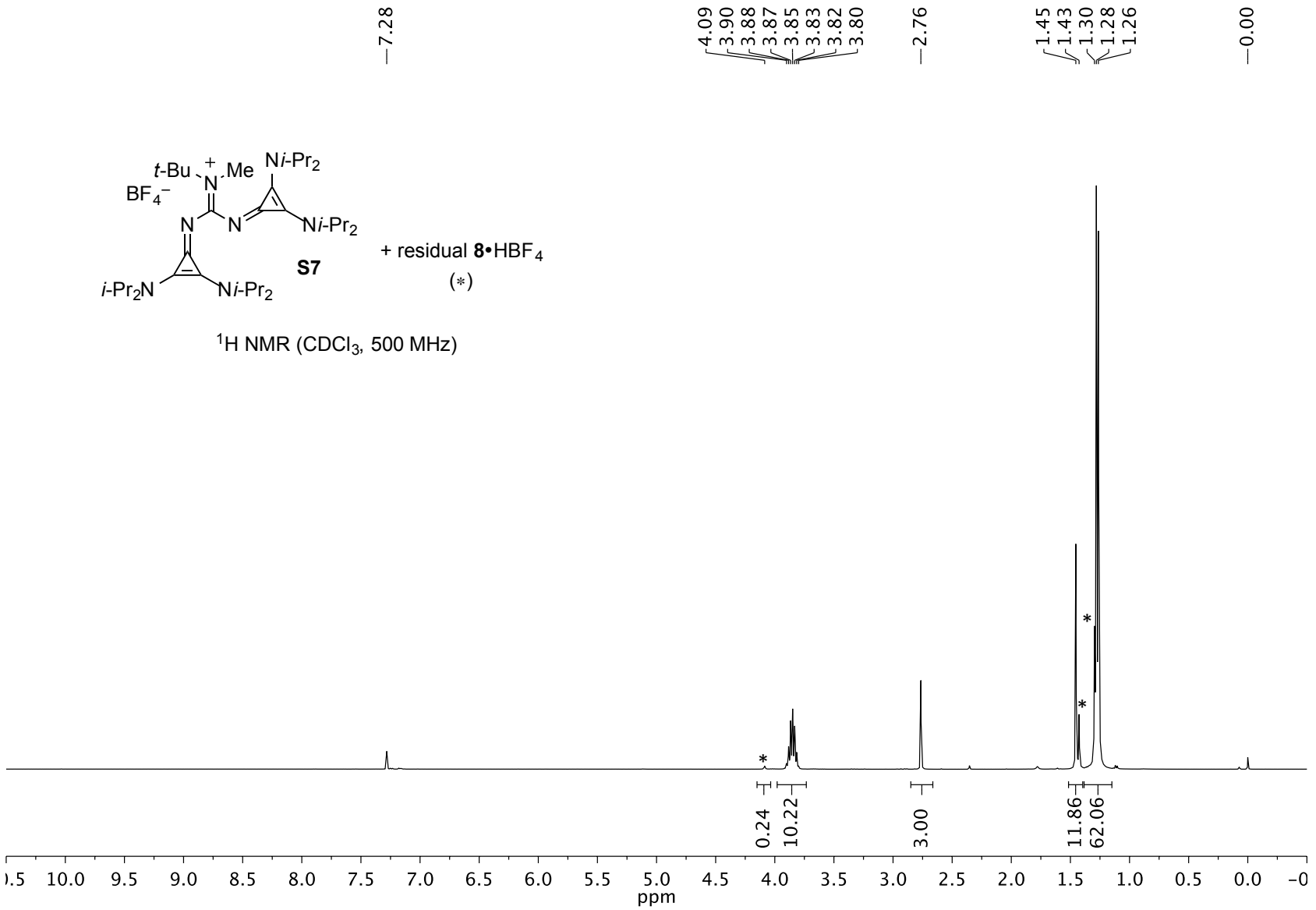
S6

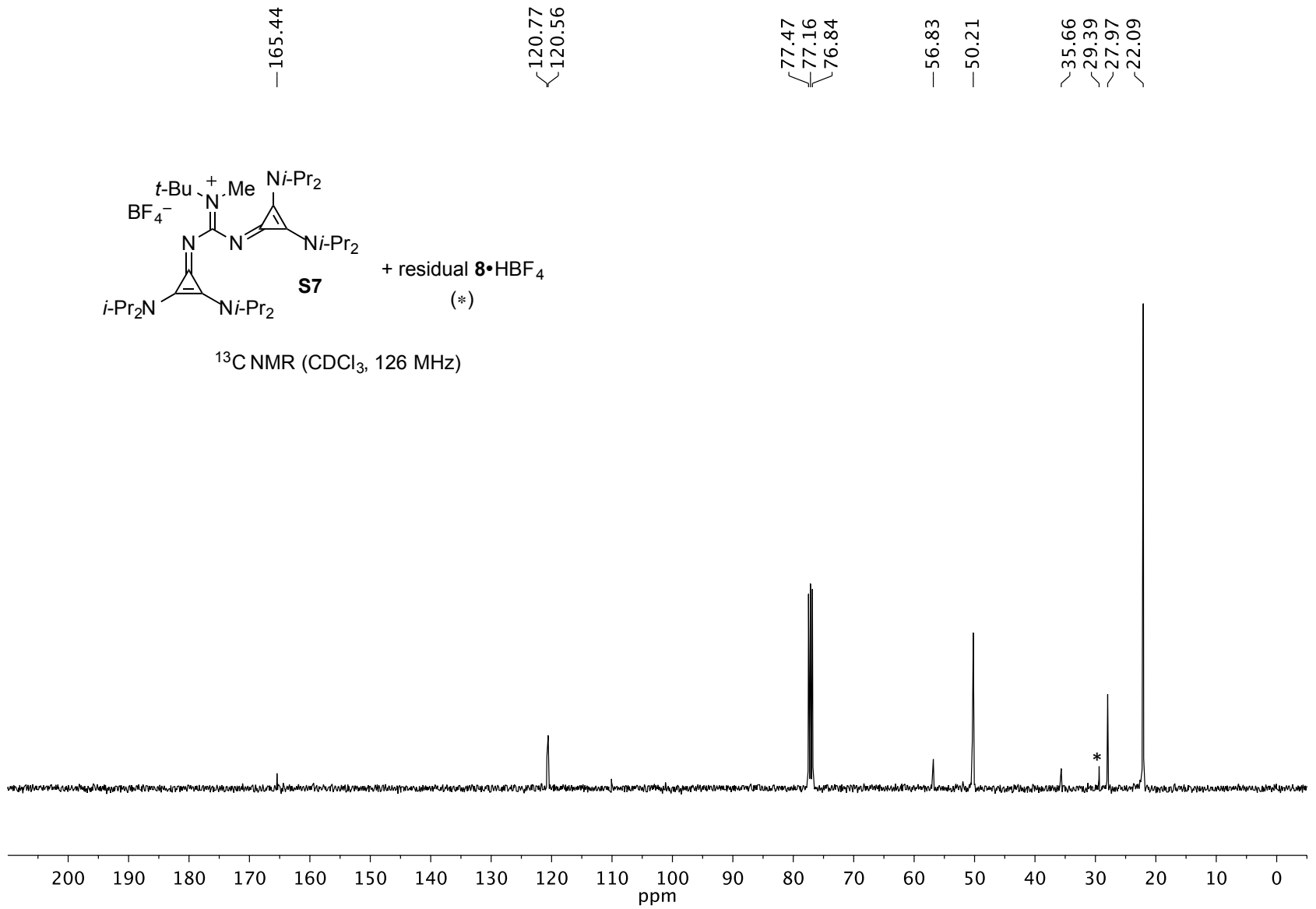
^{1}H NMR ($CDCl_3$, 500 MHz)

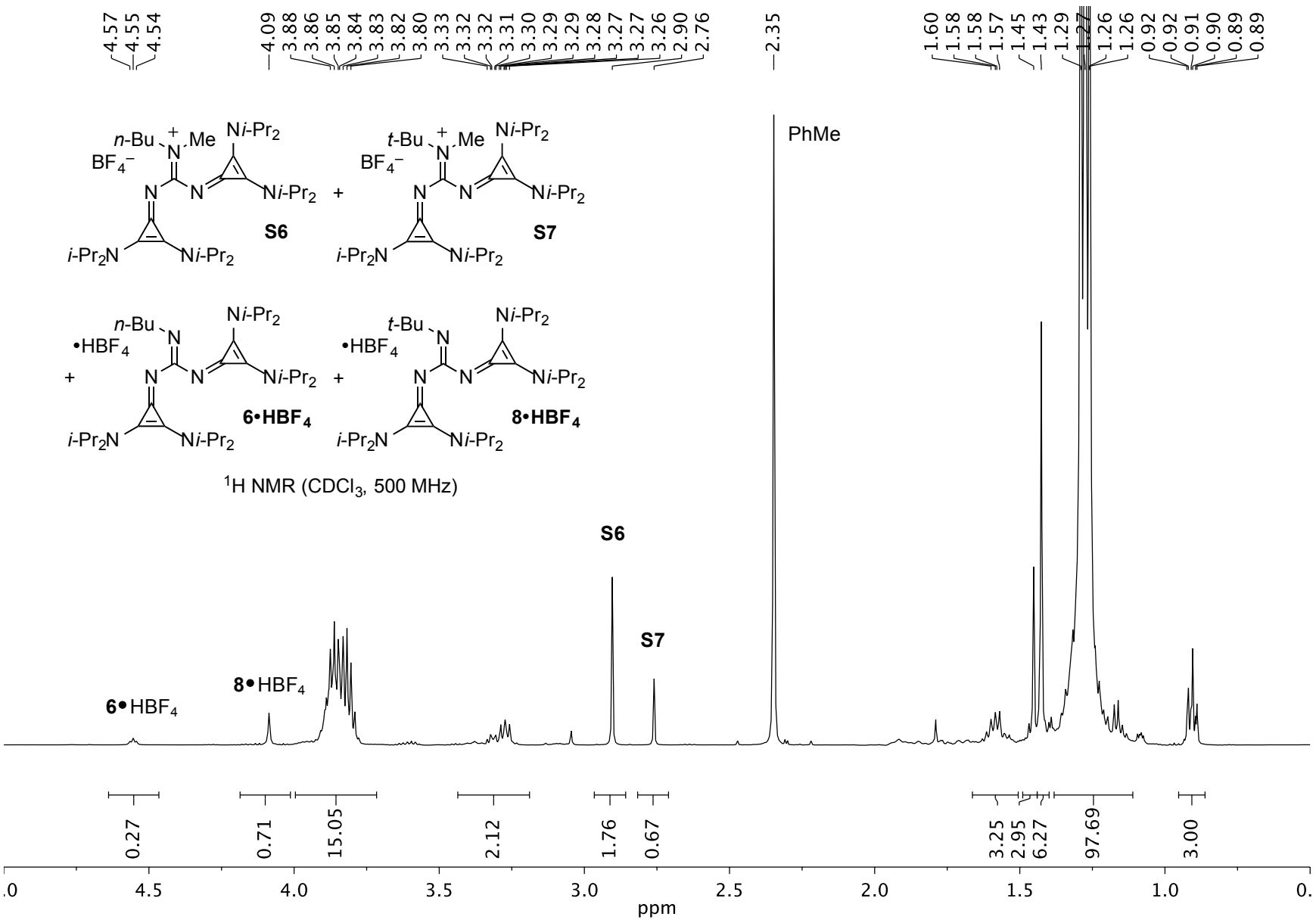


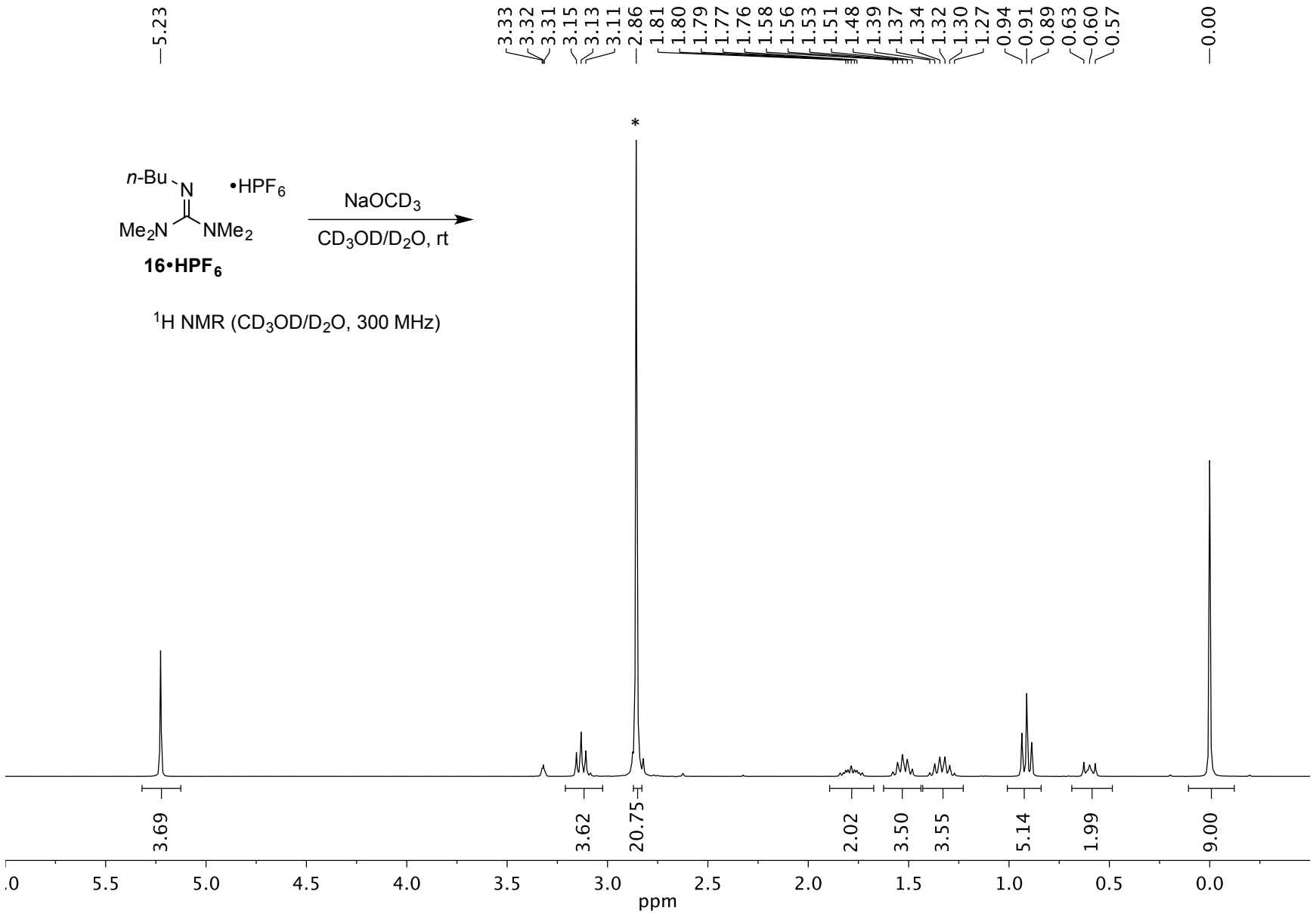
S6

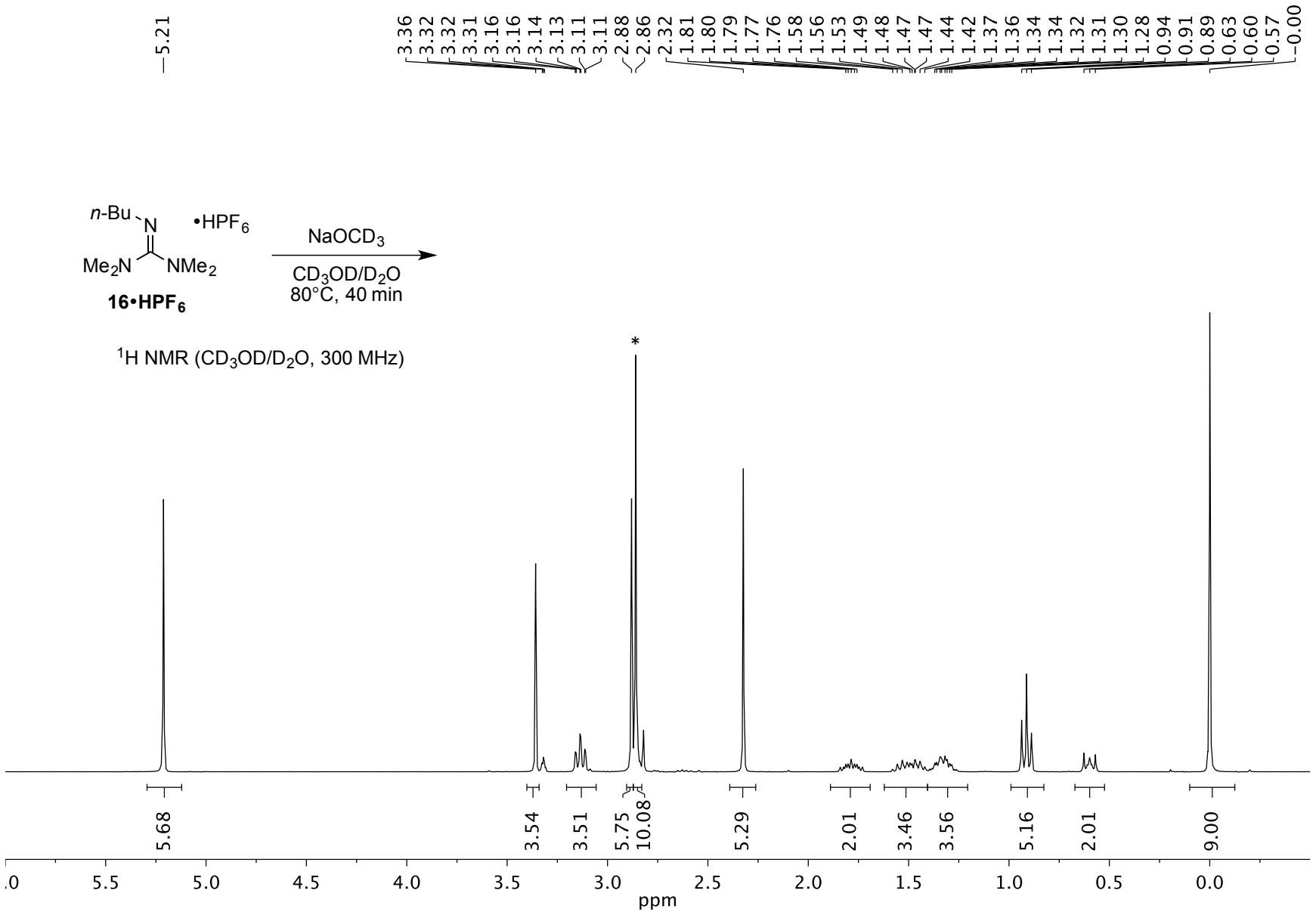
^{13}C NMR ($CDCl_3$, 126 MHz)

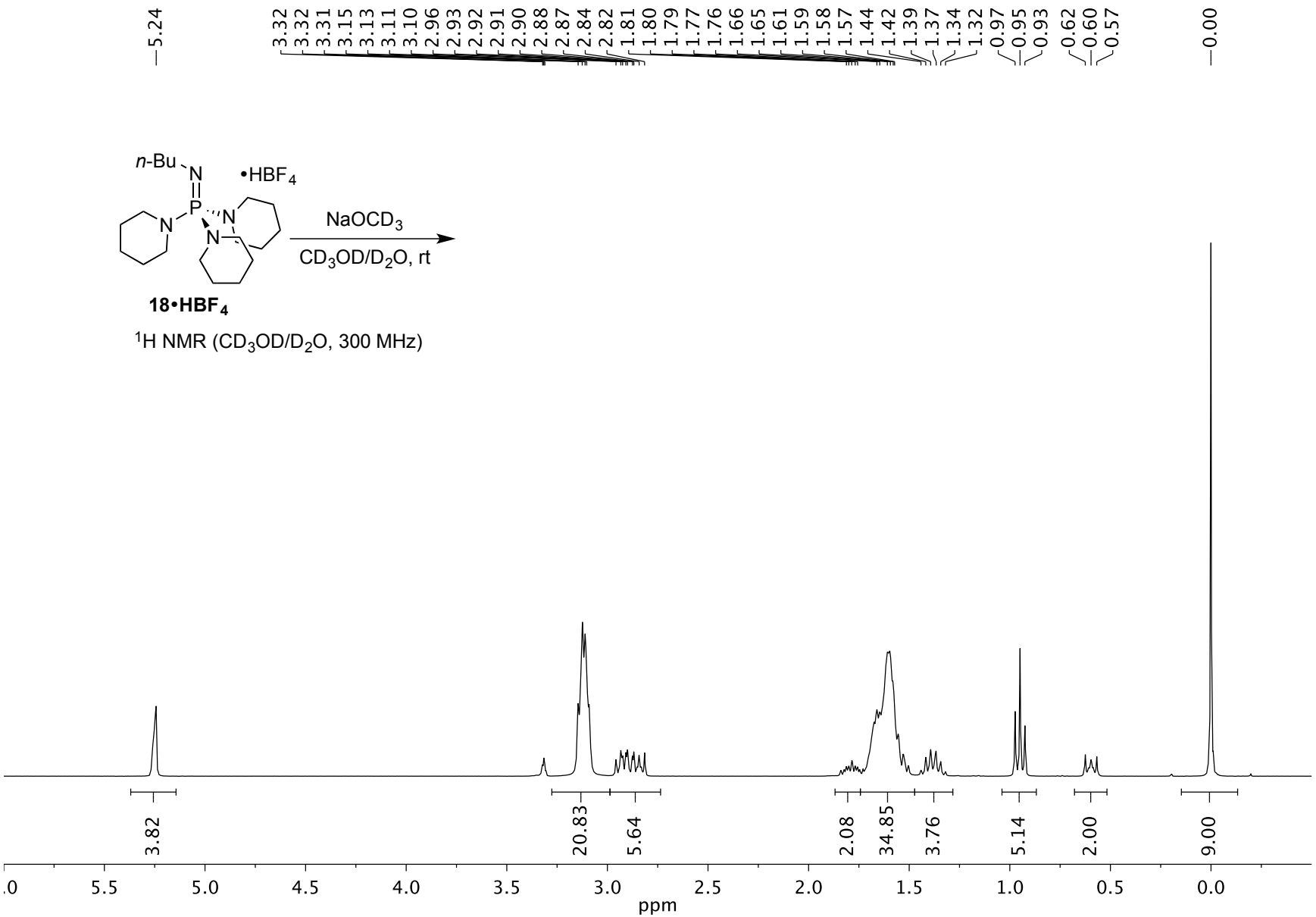

7.28
4.09
3.90
3.88
3.87
3.85
3.83
3.82
3.80
2.76
1.45
1.43
1.30
1.28
1.26
0.00
t-Bu
Me
Ni-Pr2
BF4−
Ni-Pr2
i-Pr2N
Ni-Pr2
S7
+ residual 8•HBF4
(*)
1H NMR (CDCl3, 500 MHz)
0.24
10.22
3.00
11.86
62.06
ppm

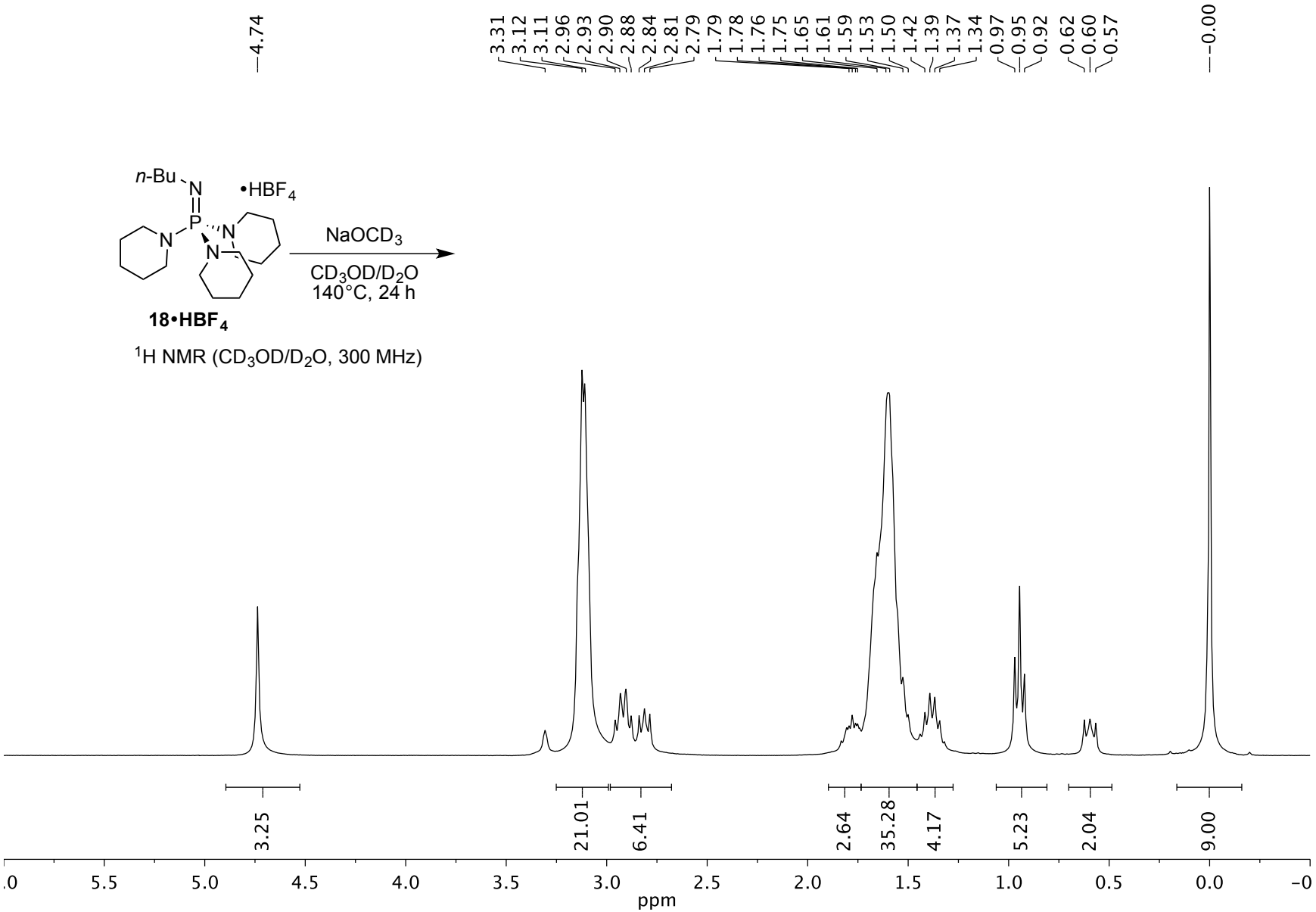

165.44
120.77
120.56
77.47
77.16
76.84
56.83
50.21
35.66
29.39
27.97
22.09
t-Bu
Me
N
BF4−
Ni-Pr2
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
S7
+ residual 8•HBF4
(*)
13C NMR (CDCl3, 126 MHz)
*
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

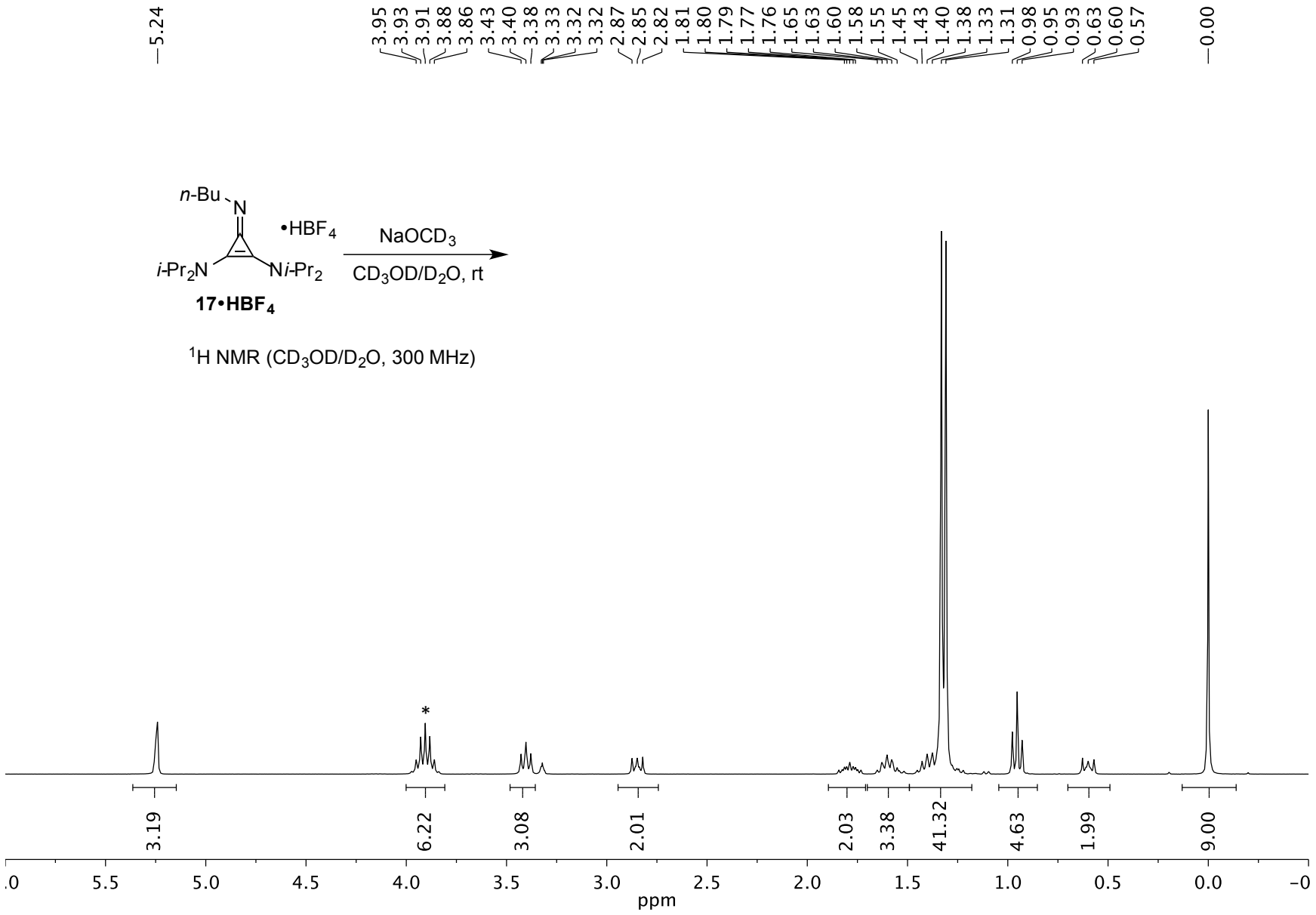

4.57
4.55
4.54
4.09
3.88
3.86
3.85
3.84
3.83
3.82
3.80
3.33
3.32
3.32
3.31
3.30
3.29
3.29
3.28
3.27
3.27
3.26
2.90
2.76
2.35
1.60
1.58
1.58
1.57
1.45
1.43
1.29
1.27
1.26
1.26
0.92
0.92
0.91
0.90
0.89
0.89
n-Bu
Me
BF4−
Ni-Pr2
i-Pr2N
S6
t-Bu
S7
•HBF4
6•HBF4
8•HBF4
1H NMR (CDCl3, 500 MHz)
PhMe
S6
S7
8•HBF4
6•HBF4
0.27
0.71
15.05
2.12
1.76
0.67
3.25
2.95
6.27
97.69
3.00
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

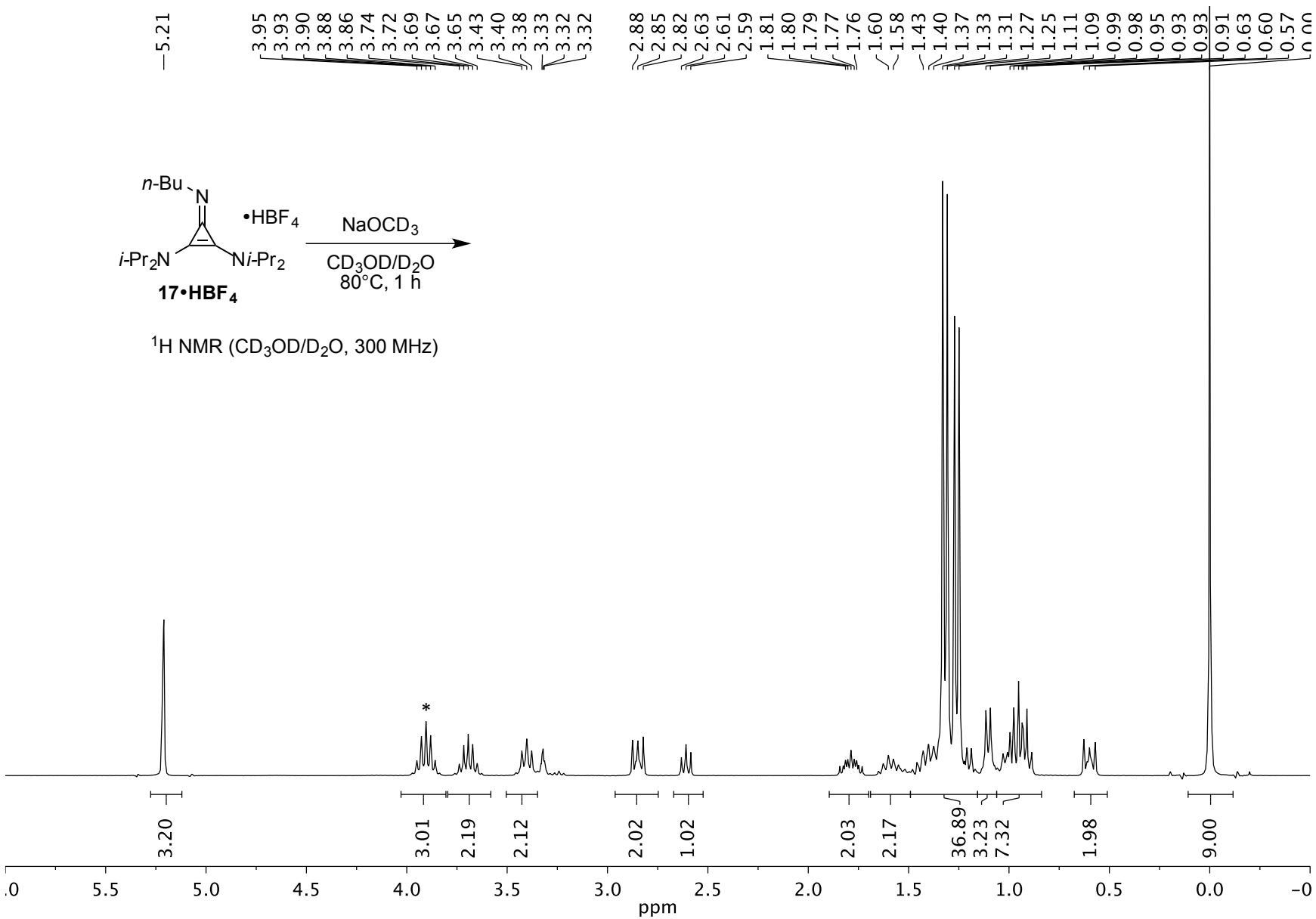

5.23
3.33
3.32
3.31
3.15
3.13
3.11
2.86
1.81
1.80
1.79
1.77
1.76
1.58
1.56
1.53
1.51
1.48
1.39
1.37
1.34
1.32
1.30
1.27
0.94
0.91
0.89
0.63
0.60
0.57
0.00
*
n-Bu
N
•HPF6
Me2N
NMe2
16•HPF6
NaOCD3
CD3OD/D2O, rt
1H NMR (CD3OD/D2O, 300 MHz)
3.69
3.62
20.75
2.02
3.50
3.55
5.14
1.99
9.00
ppm

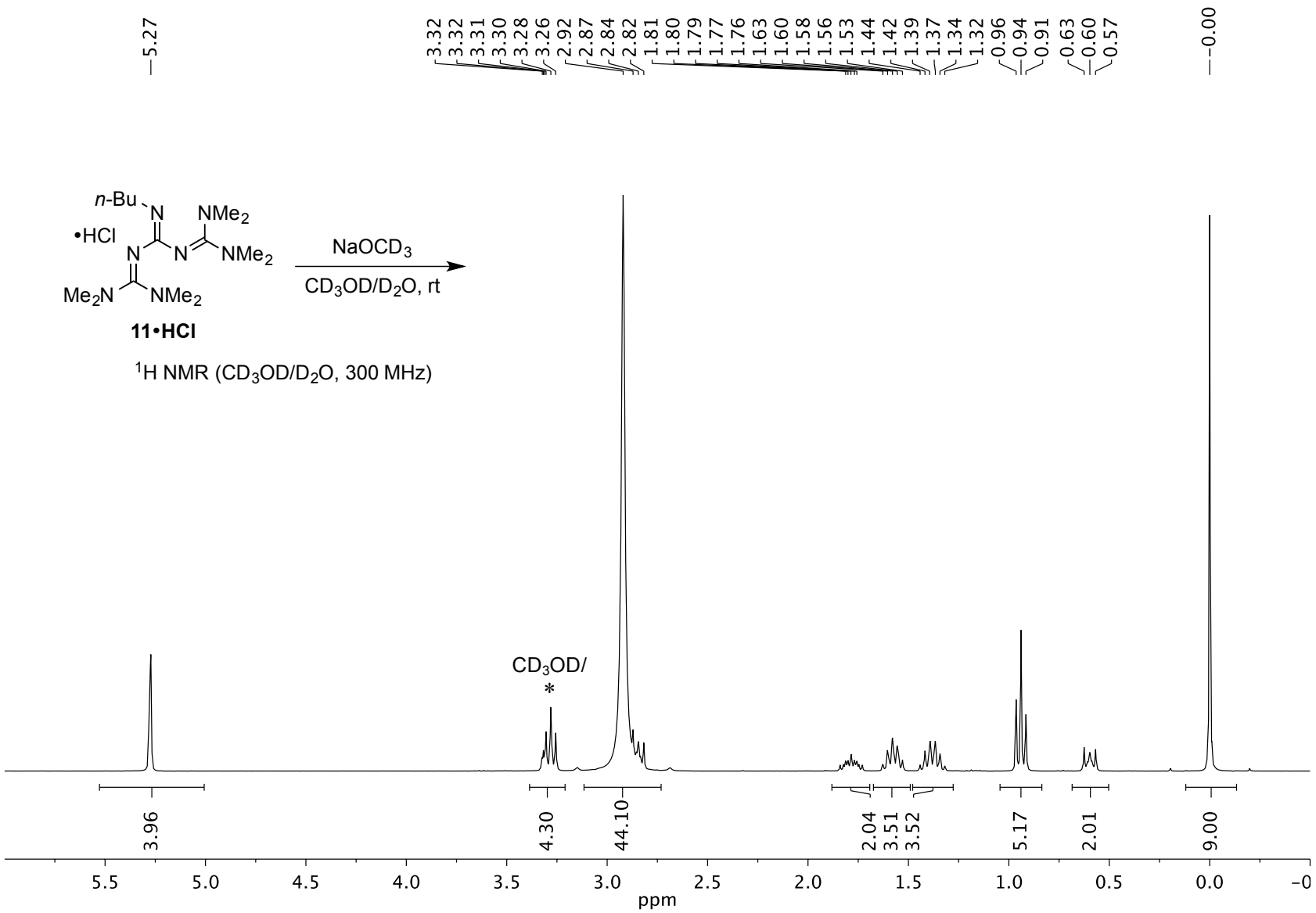

5.21
3.36
3.32
3.32
3.31
3.16
3.16
3.14
3.13
3.11
3.11
2.88
2.86
2.32
1.81
1.80
1.79
1.77
1.76
1.58
1.56
1.53
1.49
1.48
1.47
1.47
1.44
1.42
1.37
1.36
1.34
1.34
1.32
1.31
1.30
1.28
0.94
0.91
0.89
0.63
0.60
0.57
0.00
n-Bu
N
•HPF6
Me2N
NMe2
16•HPF6
NaOCD3
CD3OD/D2O
80°C, 40 min
1H NMR (CD3OD/D2O, 300 MHz)
*
5.68
3.54
3.51
5.75
10.08
5.29
2.01
3.46
3.56
5.16
2.01
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

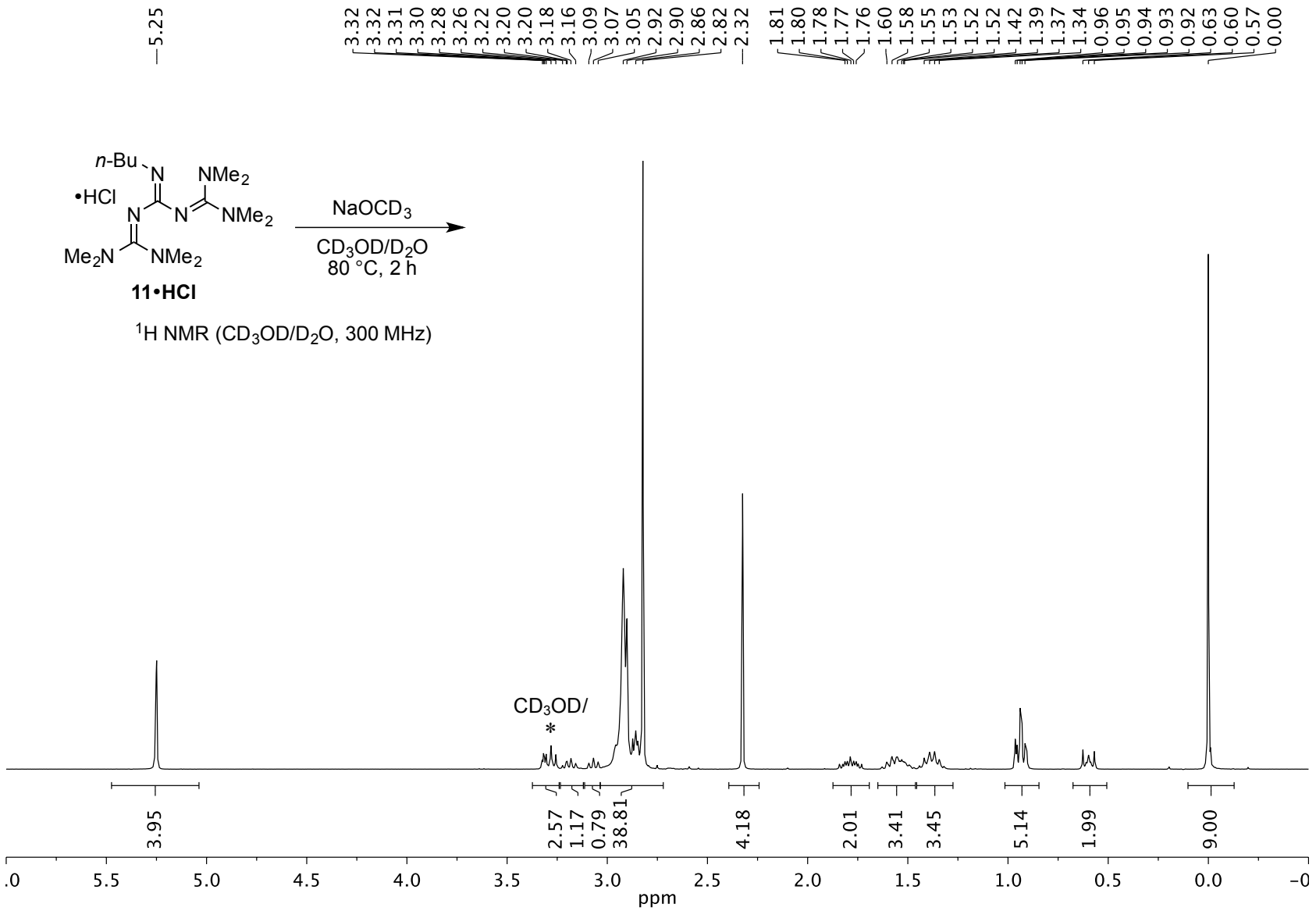

5.24
3.32
3.32
3.31
3.15
3.13
3.11
3.10
2.96
2.93
2.92
2.91
2.90
2.88
2.87
2.84
2.82
1.81
1.80
1.79
1.77
1.76
1.66
1.65
1.61
1.59
1.58
1.57
1.44
1.42
1.39
1.37
1.34
1.32
0.97
0.95
0.93
0.62
0.60
0.57
0.00
n-Bu
N
•HBF4
P
N
N
N
NaOCD3
CD3OD/D2O, rt
18•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
3.82
20.83
5.64
2.08
34.85
3.76
5.14
2.00
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

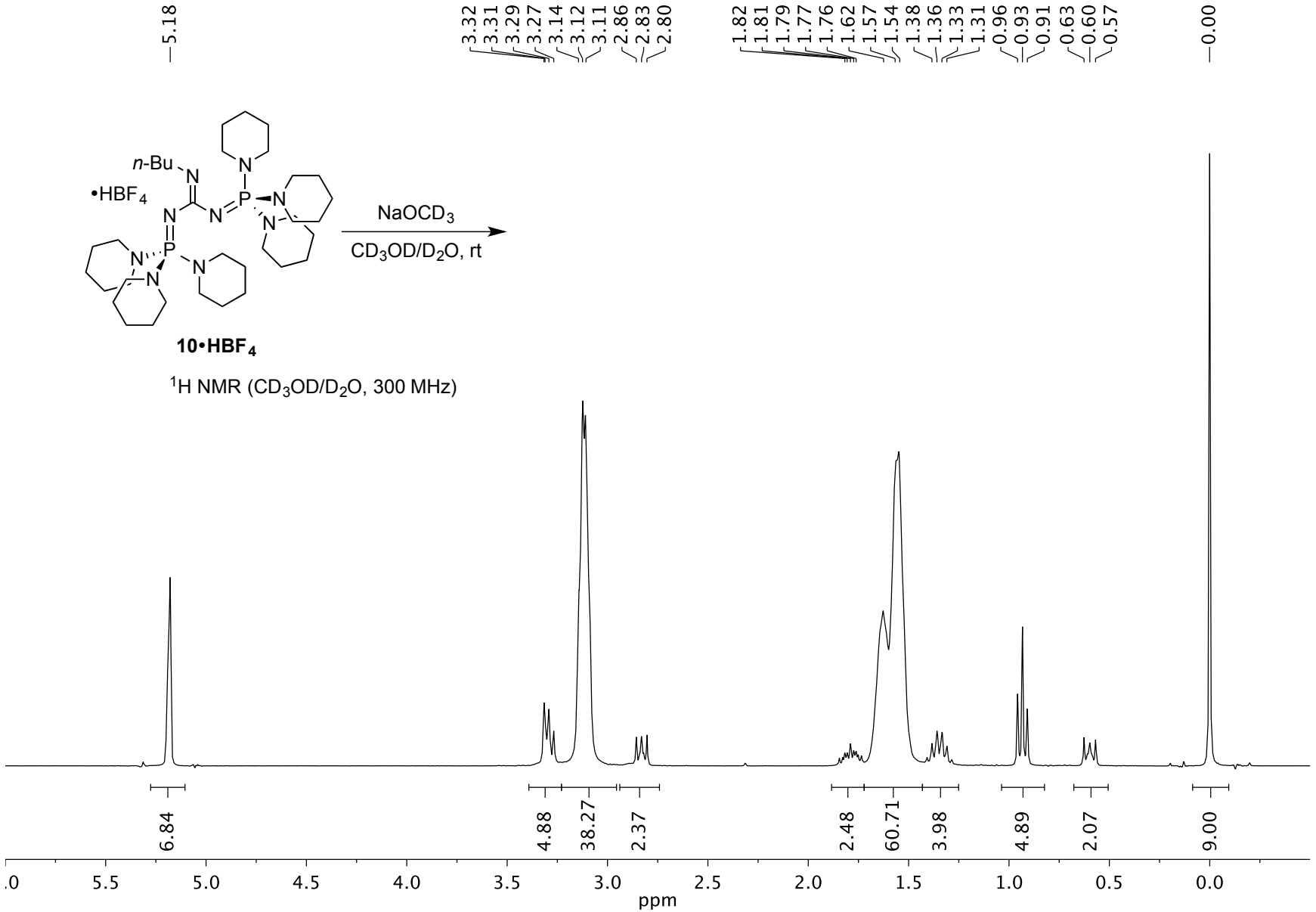

4.74
3.31
3.12
3.11
2.96
2.93
2.90
2.88
2.84
2.81
2.79
1.79
1.78
1.76
1.75
1.65
1.61
1.59
1.53
1.50
1.42
1.39
1.37
1.34
0.97
0.95
0.92
0.62
0.60
0.57
0.00
n-Bu
N
•HBF4
P
N
N
N
NaOCD3
CD3OD/D2O
140°C, 24 h
18•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
3.25
21.01
6.41
2.64
35.28
4.17
5.23
2.04
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

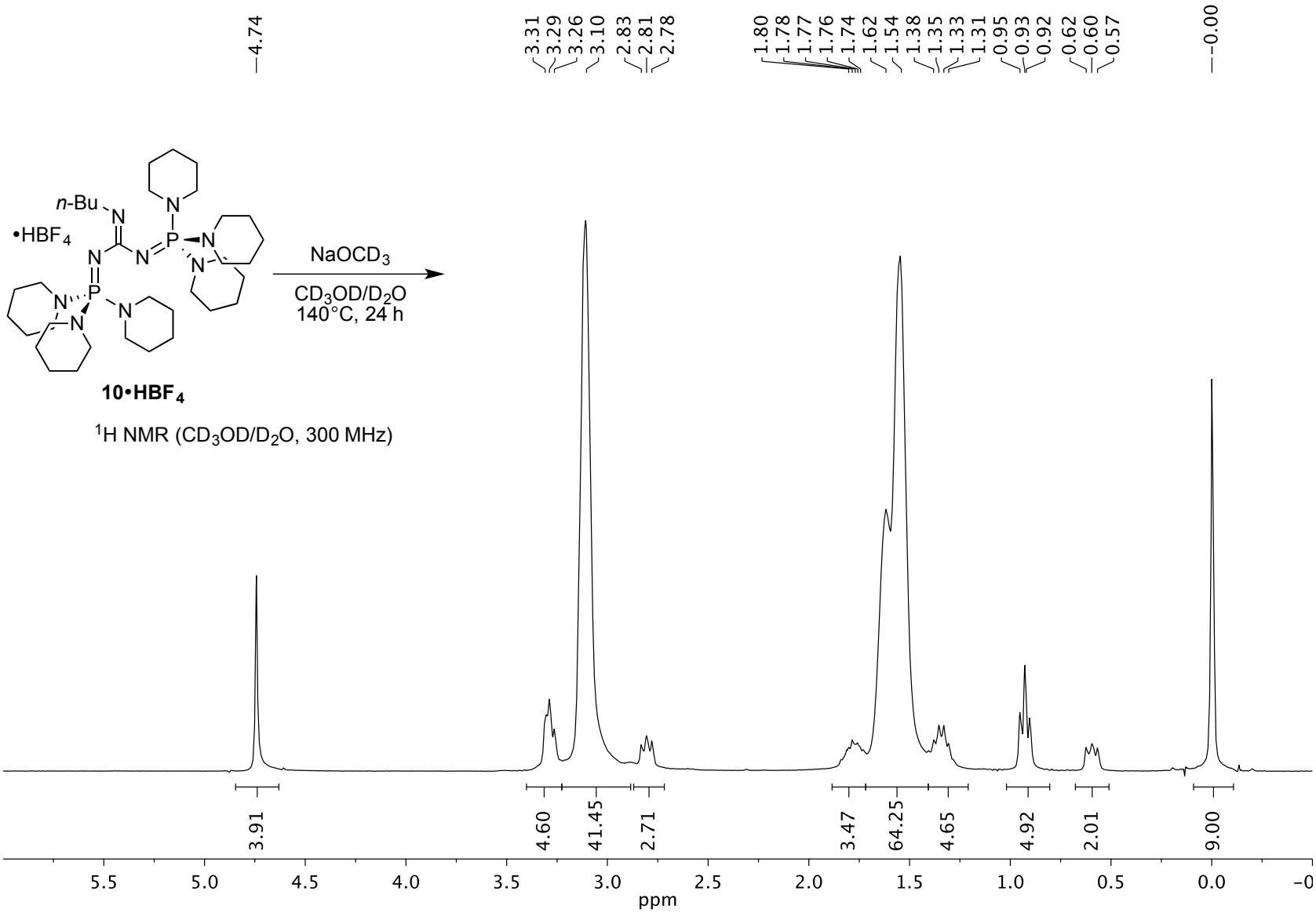

5.24
3.95
3.93
3.91
3.88
3.86
3.43
3.40
3.38
3.33
3.32
3.32
2.87
2.85
2.82
1.81
1.80
1.79
1.77
1.76
1.65
1.63
1.60
1.58
1.55
1.45
1.43
1.40
1.38
1.33
1.31
0.98
0.95
0.93
0.63
0.60
0.57
0.00
n-Bu
N
•HBF4
i-Pr2N
Ni-Pr2
NaOCD3
CD3OD/D2O, rt
17•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
*
3.19
6.22
3.08
2.01
2.03
3.38
41.32
4.63
1.99
9.00
ppm

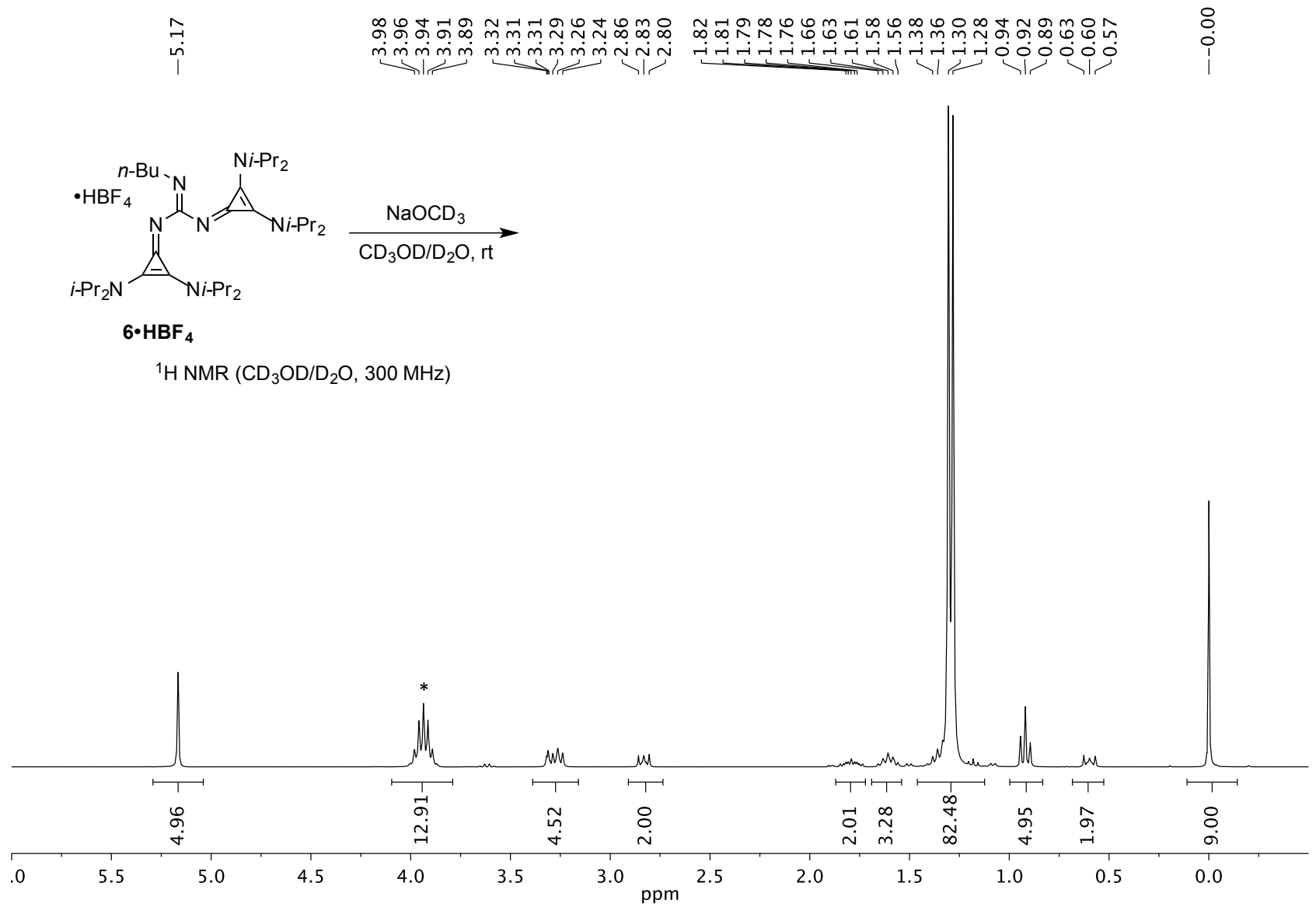

n-Bu
N
•HBF4
i-Pr2N
Ni-Pr2
17•HBF4
NaOCD3
CD3OD/D2O
80°C, 1 h
1H NMR (CD3OD/D2O, 300 MHz)
5.21
3.95
3.93
3.90
3.88
3.86
3.74
3.72
3.69
3.67
3.65
3.43
3.40
3.38
3.33
3.32
3.32
2.88
2.85
2.82
2.63
2.61
2.59
1.81
1.80
1.79
1.77
1.76
1.60
1.58
1.43
1.40
1.37
1.33
1.31
1.27
1.25
1.11
1.09
0.99
0.98
0.95
0.93
0.93
0.91
0.63
0.60
0.57
*
3.20
3.01
2.19
2.12
2.02
1.02
2.03
2.17
36.89
3.23
7.32
1.98
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


5.27
3.32
3.32
3.31
3.30
3.28
3.26
2.92
2.87
2.84
2.82
1.81
1.80
1.79
1.77
1.76
1.63
1.60
1.58
1.56
1.53
1.44
1.42
1.39
1.37
1.34
1.32
0.96
0.94
0.91
0.63
0.60
0.57
0.00
n-Bu
NMe2
•HCl
N
N
NMe2
NMe2
Me2N
NMe2
NaOCD3
CD3OD/D2O, rt
11•HCl
1H NMR (CD3OD/D2O, 300 MHz)
CD3OD/
*
3.96
4.30
44.10
2.04
3.51
3.52
5.17
2.01
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm


5.25
3.32
3.32
3.31
3.30
3.28
3.26
3.22
3.20
3.20
3.18
3.16
3.09
3.07
3.05
2.92
2.90
2.86
2.82
2.32
1.81
1.80
1.78
1.77
1.76
1.60
1.58
1.55
1.53
1.52
1.52
1.42
1.39
1.37
1.34
0.96
0.95
0.94
0.93
0.92
0.63
0.60
0.57
0.00
n-Bu
NMe2
•HCl
N
N
N
NMe2
Me2N
NMe2
NaOCD3
CD3OD/D2O
80 °C, 2 h
11•HCl
1H NMR (CD3OD/D2O, 300 MHz)
CD3OD/
*
3.95
2.57
1.17
0.79
38.81
4.18
2.01
3.41
3.45
5.14
1.99
9.00
.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm

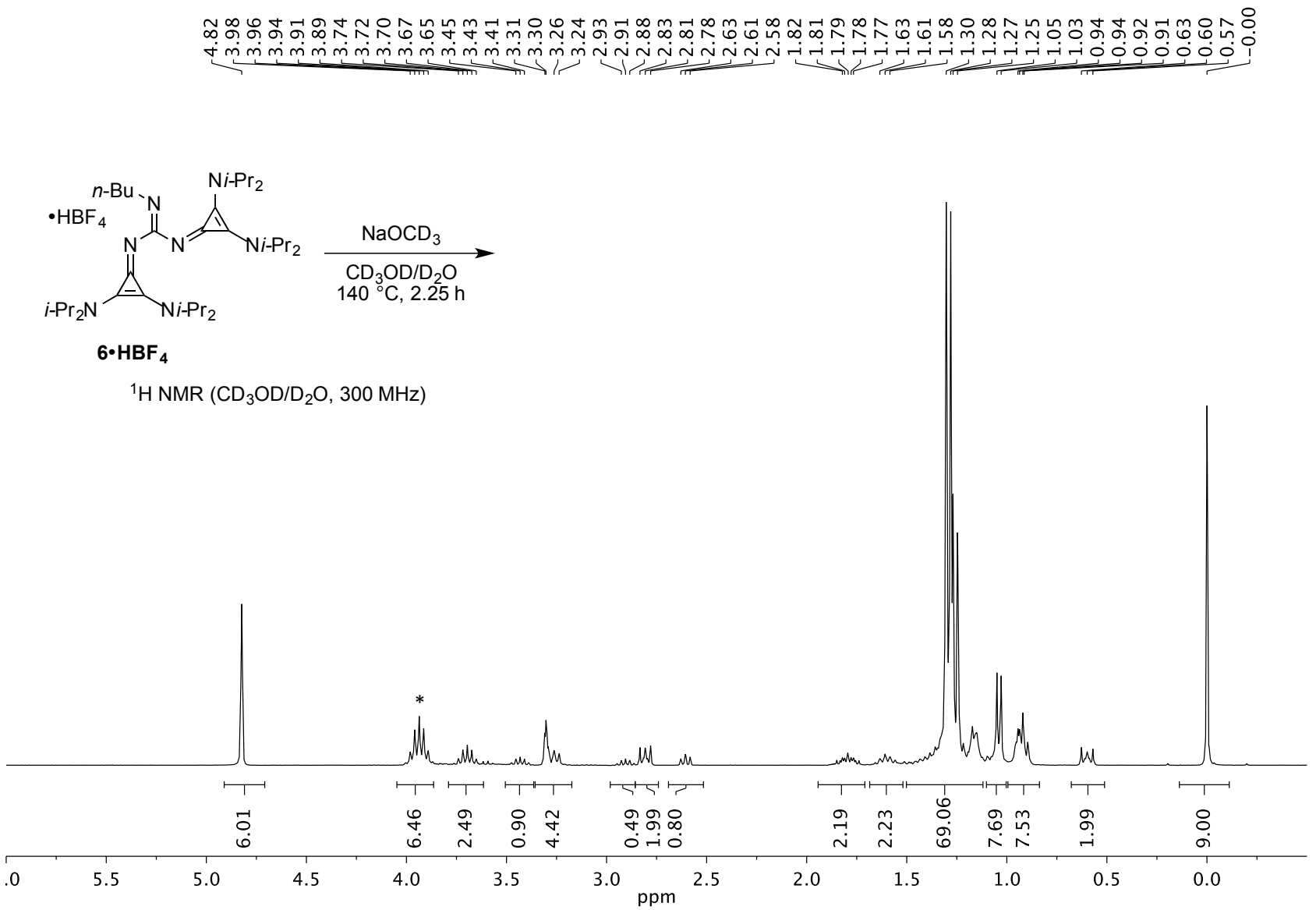

5.18
3.32
3.31
3.29
3.27
3.14
3.12
3.11
2.86
2.83
2.80
1.82
1.81
1.79
1.77
1.76
1.62
1.57
1.54
1.38
1.36
1.33
1.31
0.96
0.93
0.91
0.63
0.60
0.57
0.00
n-Bu
•HBF4
NaOCD3
CD3OD/D2O, rt
10•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
6.84
4.88
38.27
2.37
2.48
60.71
3.98
4.89
2.07
9.00
ppm

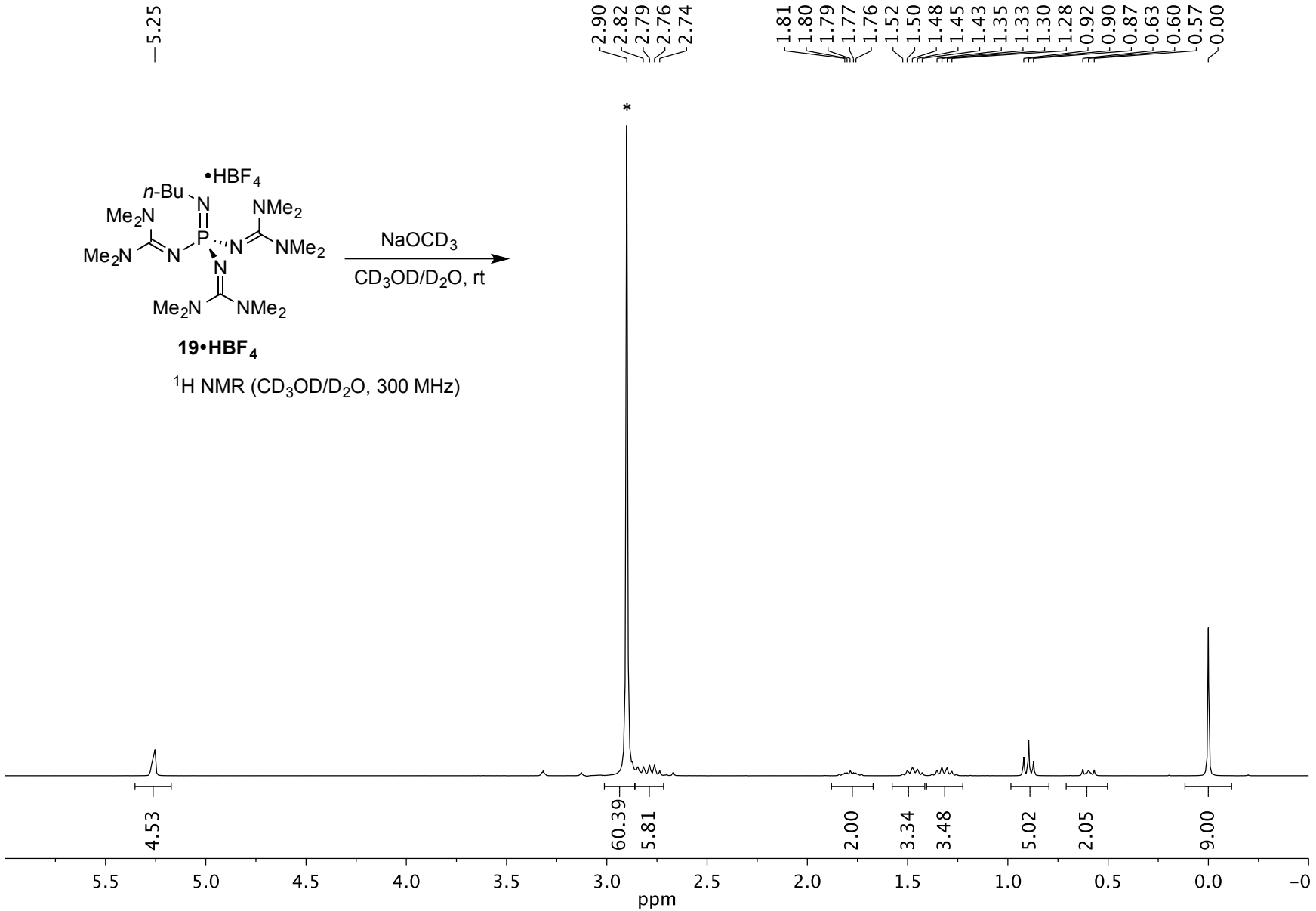

4.74
3.31
3.29
3.26
3.10
2.83
2.81
2.78
1.80
1.78
1.77
1.76
1.74
1.62
1.54
1.38
1.35
1.33
1.31
0.95
0.93
0.92
0.62
0.60
0.57
0.00
n-Bu
•HBF4
NaOCD3
CD3OD/D2O
140°C, 24 h
10•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
3.91
4.60
41.45
2.71
3.47
64.25
4.65
4.92
2.01
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm

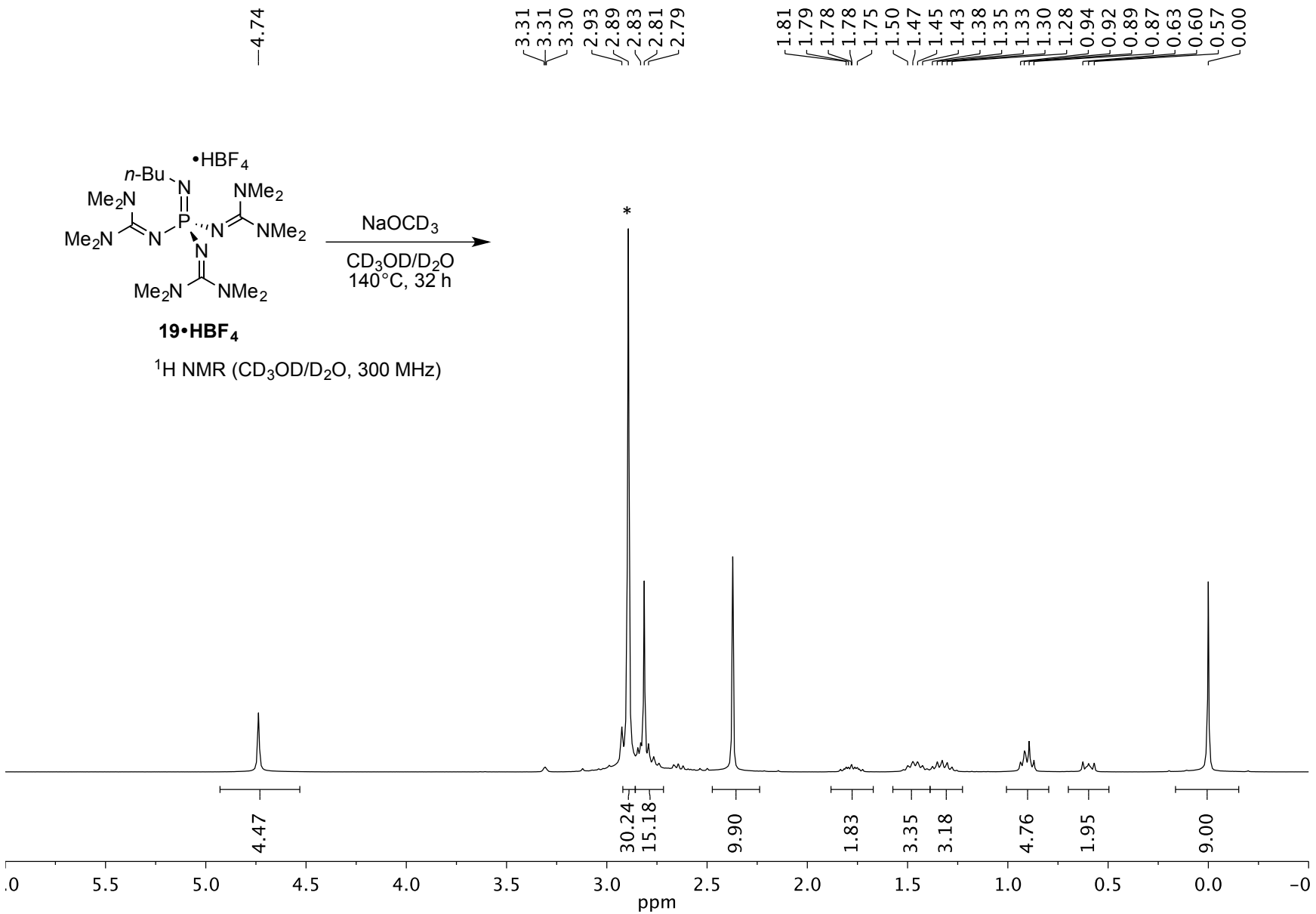


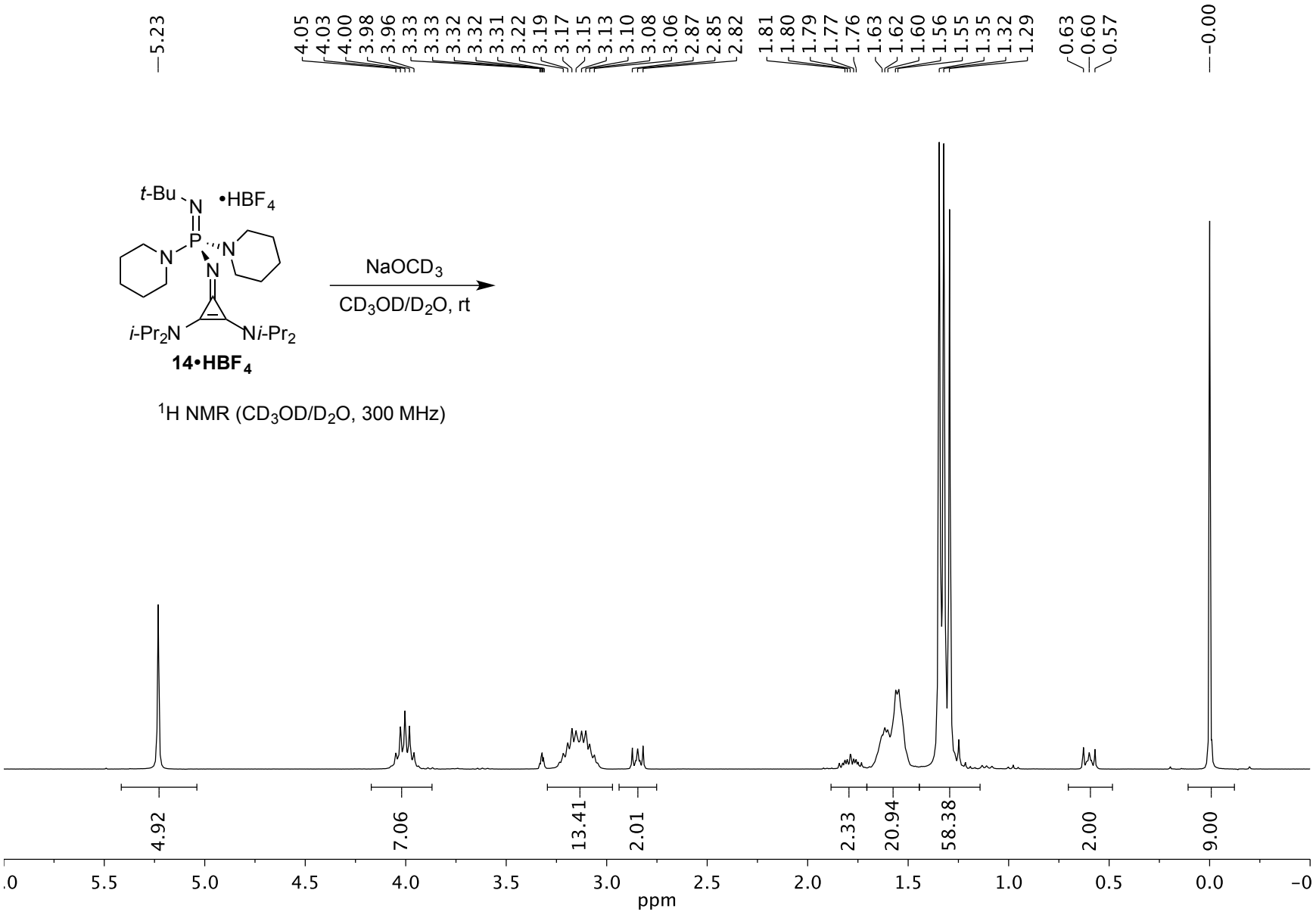
6•HBF$_4$

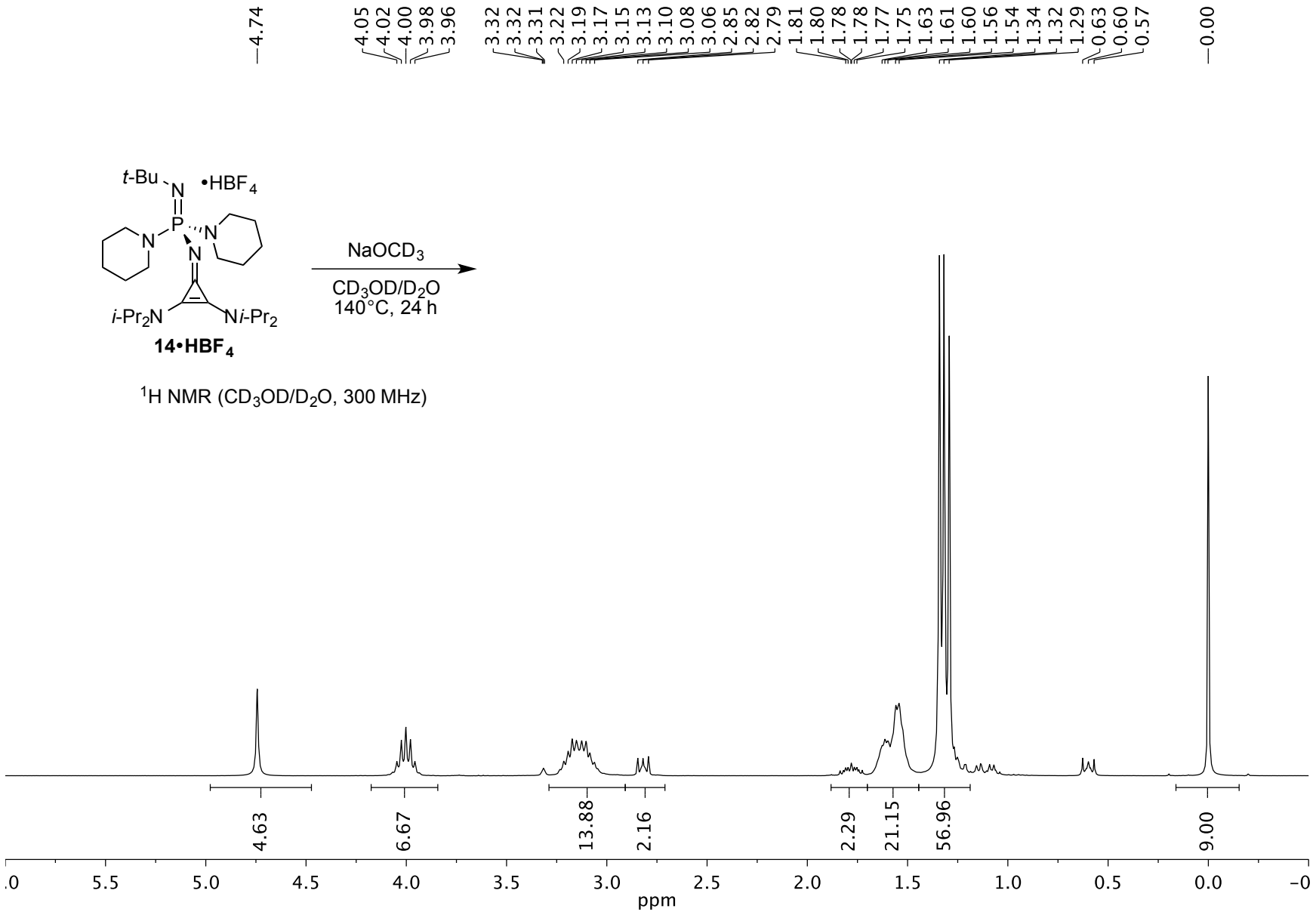
^{1}H NMR (CD_3OD/D_2O, 300 MHz)

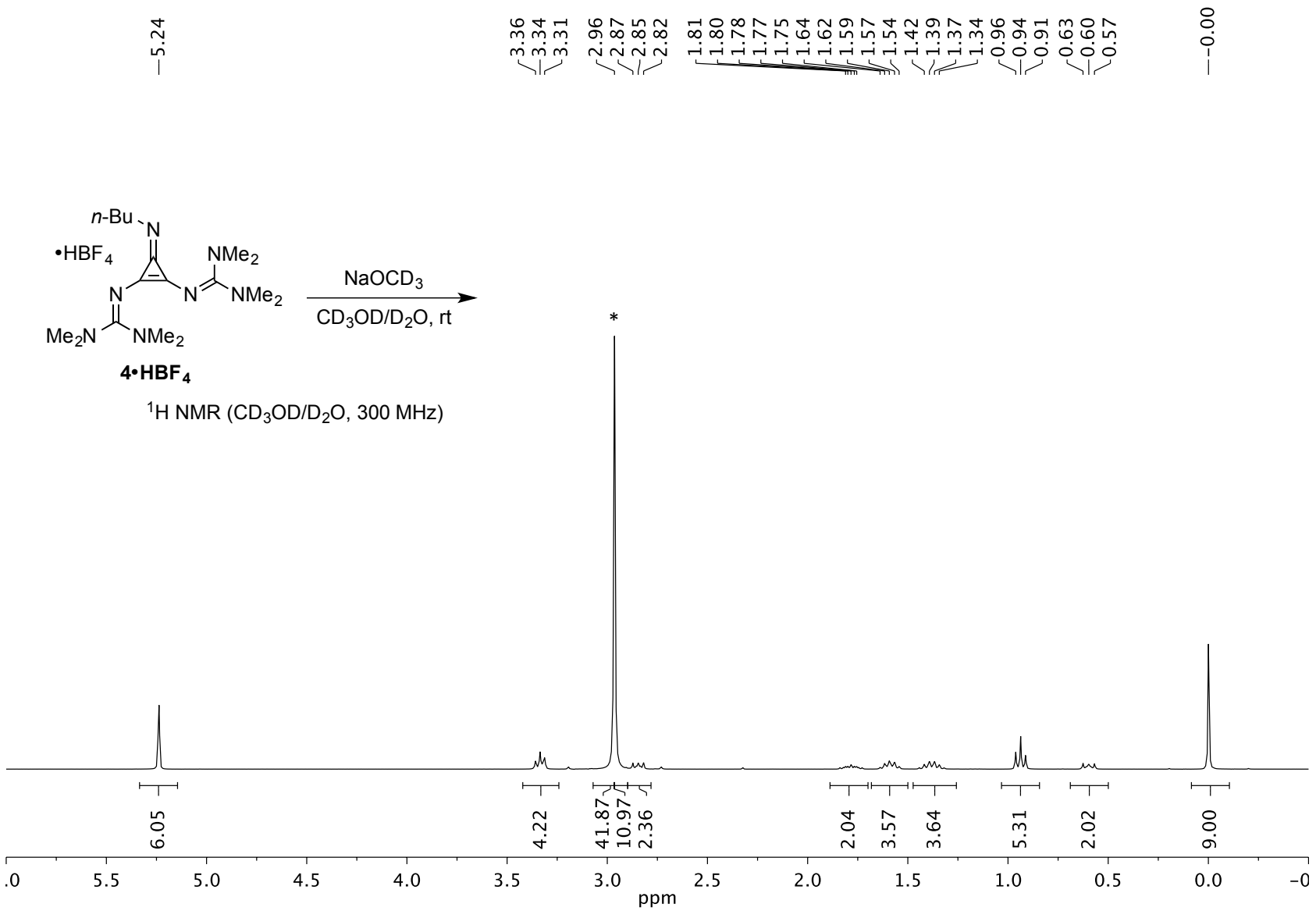

4.82
3.98
3.96
3.94
3.91
3.89
3.74
3.72
3.70
3.67
3.65
3.45
3.43
3.41
3.31
3.30
3.26
3.24
2.93
2.91
2.88
2.83
2.81
2.78
2.63
2.61
2.58
1.82
1.81
1.79
1.78
1.77
1.63
1.61
1.58
1.30
1.28
1.27
1.25
1.05
1.03
0.94
0.94
0.92
0.91
0.63
0.60
0.57
-0.00
n-Bu
•HBF4
N
N
N
N
Ni-Pr2
Ni-Pr2
i-Pr2N
Ni-Pr2
NaOCD3
CD3OD/D2O
140 °C, 2.25 h
6•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
*
6.01
6.46
2.49
0.90
4.42
0.49
1.99
0.80
2.19
2.23
69.06
7.69
7.53
1.99
9.00
.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

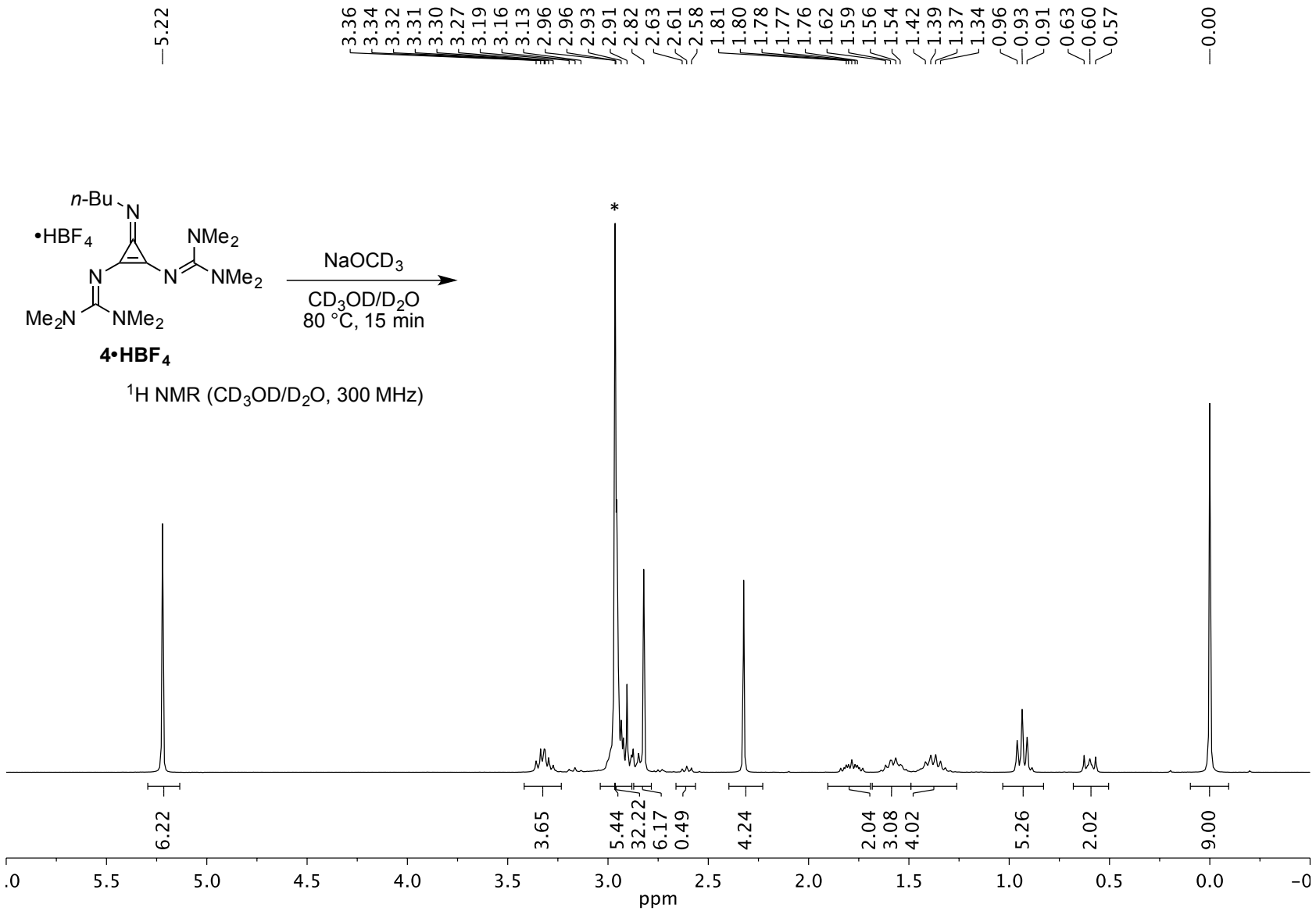

5.25
2.90
2.82
2.79
2.76
2.74
1.81
1.80
1.79
1.77
1.76
1.52
1.50
1.48
1.45
1.43
1.35
1.33
1.30
1.28
0.92
0.90
0.87
0.63
0.60
0.57
0.00
*
•HBF4
n-Bu
Me2N
NMe2
Me2N
N
P
N
NMe2
N
Me2N
NMe2
NaOCD3
CD3OD/D2O, rt
19•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
4.53
60.39
5.81
2.00
3.34
3.48
5.02
2.05
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
ppm

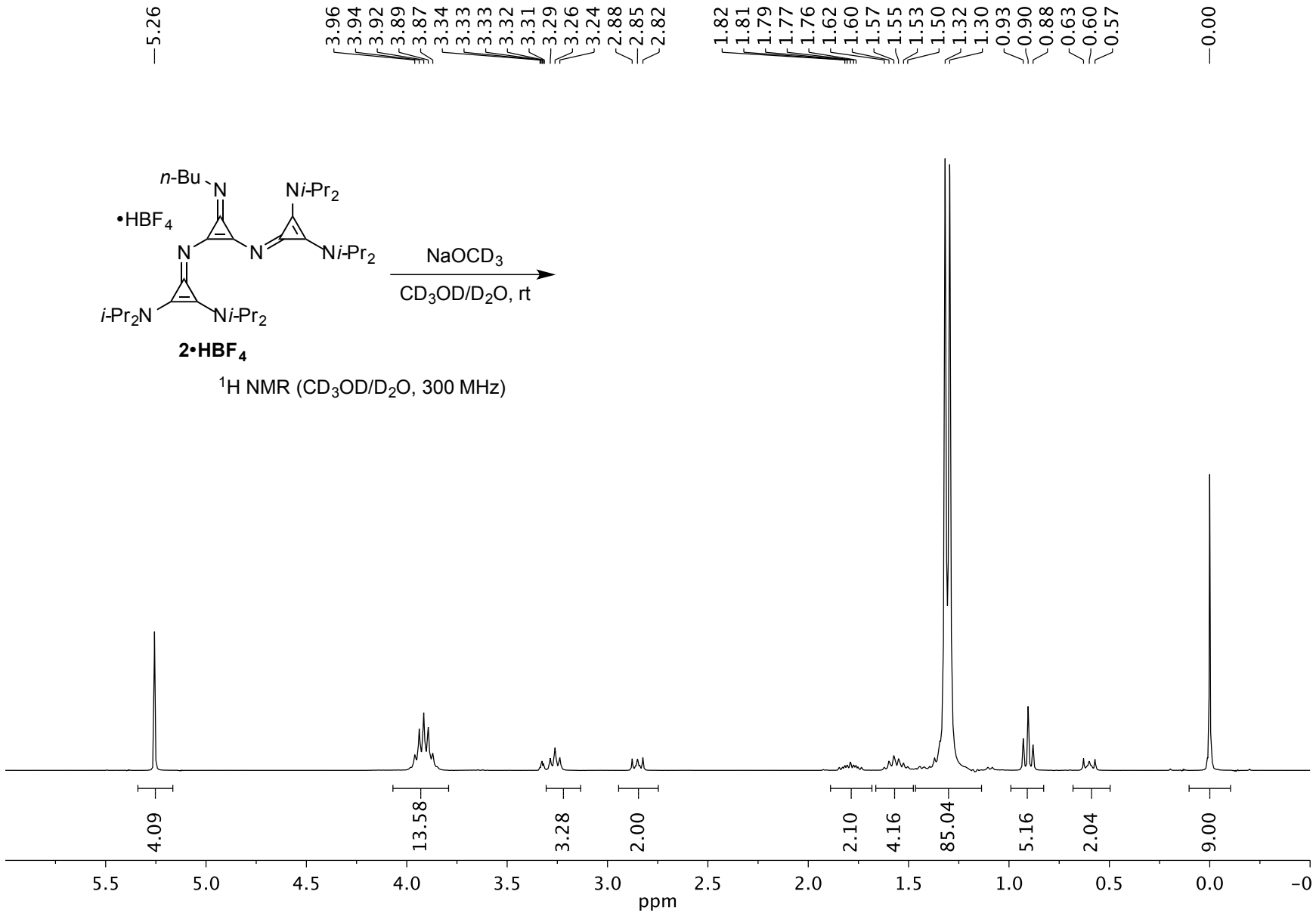

4.74
3.31
3.31
3.30
2.93
2.89
2.83
2.81
2.79
1.81
1.79
1.78
1.78
1.75
1.50
1.47
1.45
1.43
1.38
1.35
1.33
1.30
1.28
0.94
0.92
0.89
0.87
0.63
0.60
0.57
0.00
•HBF4
n-Bu
Me2N
NMe2
Me2N
N
P
N
NMe2
N
Me2N
NMe2
NaOCD3
CD3OD/D2O
140°C, 32 h
19•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
*
4.47
30.24
15.18
9.90
1.83
3.35
3.18
4.76
1.95
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

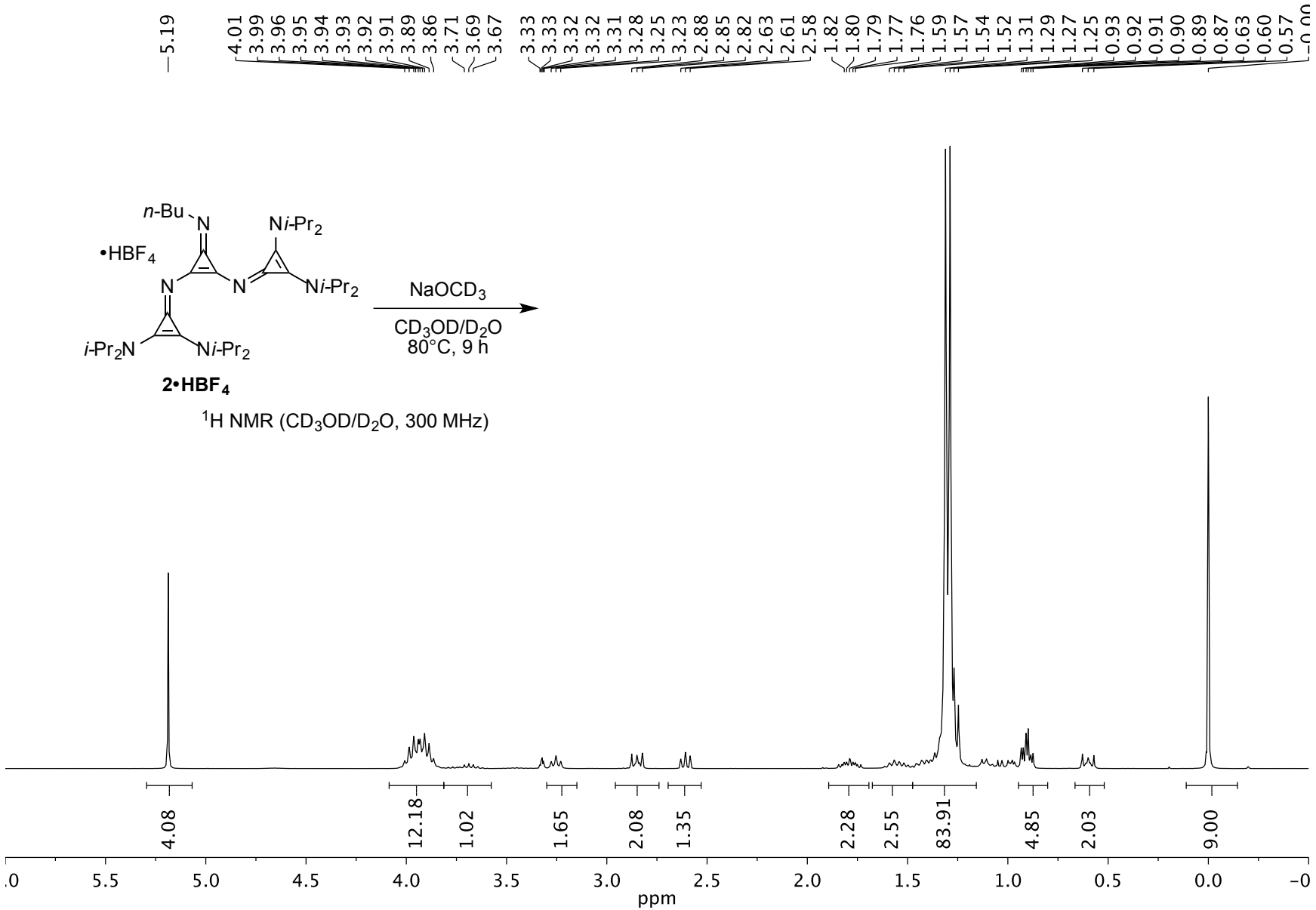

5.23
4.05
4.03
4.00
3.98
3.96
3.33
3.33
3.32
3.32
3.31
3.22
3.19
3.17
3.15
3.13
3.10
3.08
3.06
2.87
2.85
2.82
1.81
1.80
1.79
1.77
1.76
1.63
1.62
1.60
1.56
1.55
1.35
1.32
1.29
0.63
0.60
0.57
0.00
t-Bu
•HBF4
i-Pr2N
Ni-Pr2
NaOCD3
CD3OD/D2O, rt
14•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
4.92
7.06
13.41
2.01
2.33
20.94
58.38
2.00
9.00
ppm

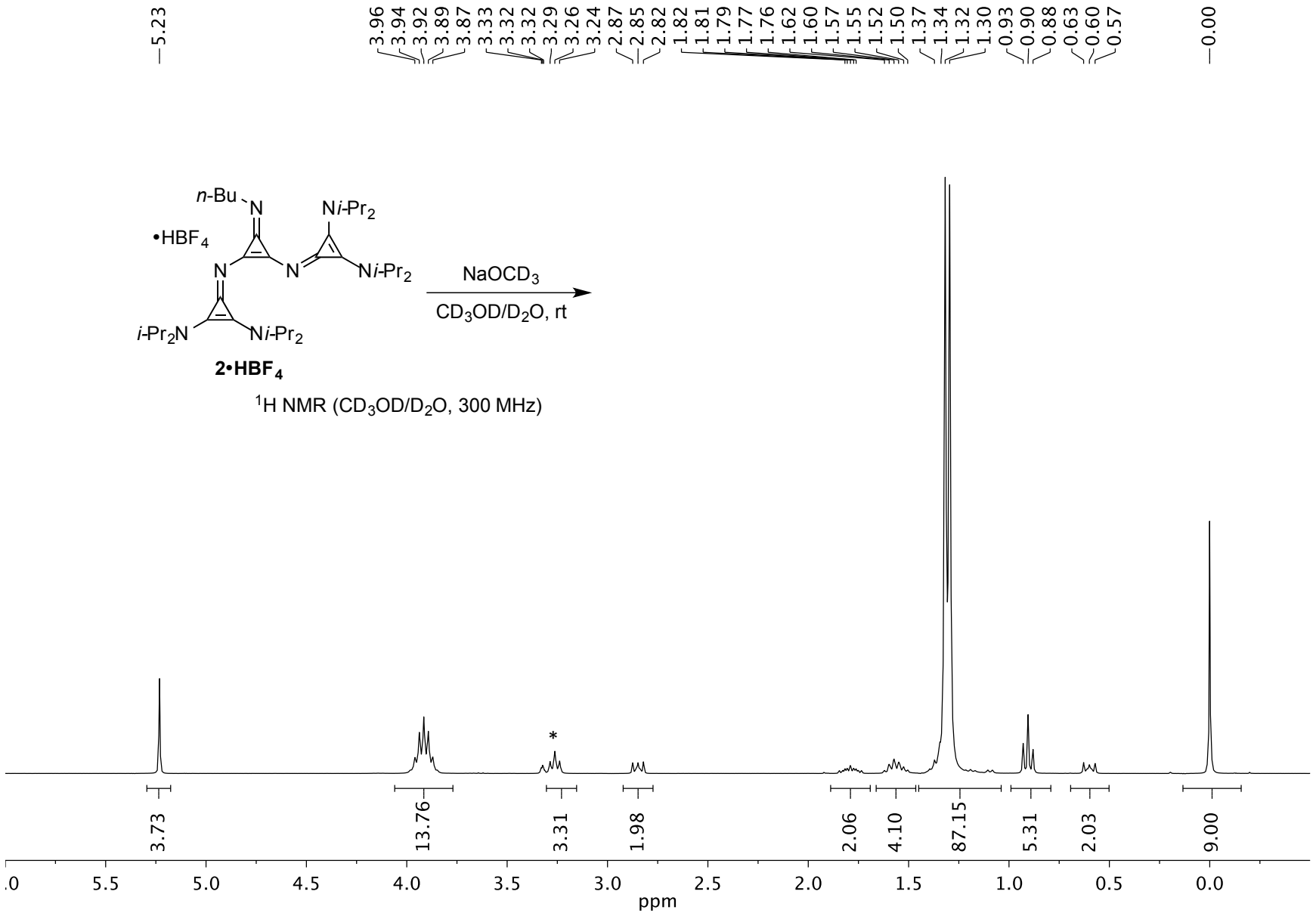

4.74
4.05
4.02
4.00
3.98
3.96
3.32
3.32
3.31
3.22
3.19
3.17
3.15
3.13
3.10
3.08
3.06
2.85
2.82
2.79
1.81
1.80
1.78
1.78
1.77
1.75
1.63
1.61
1.60
1.56
1.54
1.34
1.32
1.29
0.63
0.60
0.57
0.00
t-Bu
•HBF4
i-Pr2N
Ni-Pr2
14•HBF4
NaOCD3
CD3OD/D2O
140°C, 24 h
1H NMR (CD3OD/D2O, 300 MHz)
4.63
6.67
13.88
2.16
2.29
21.15
56.96
9.00
ppm

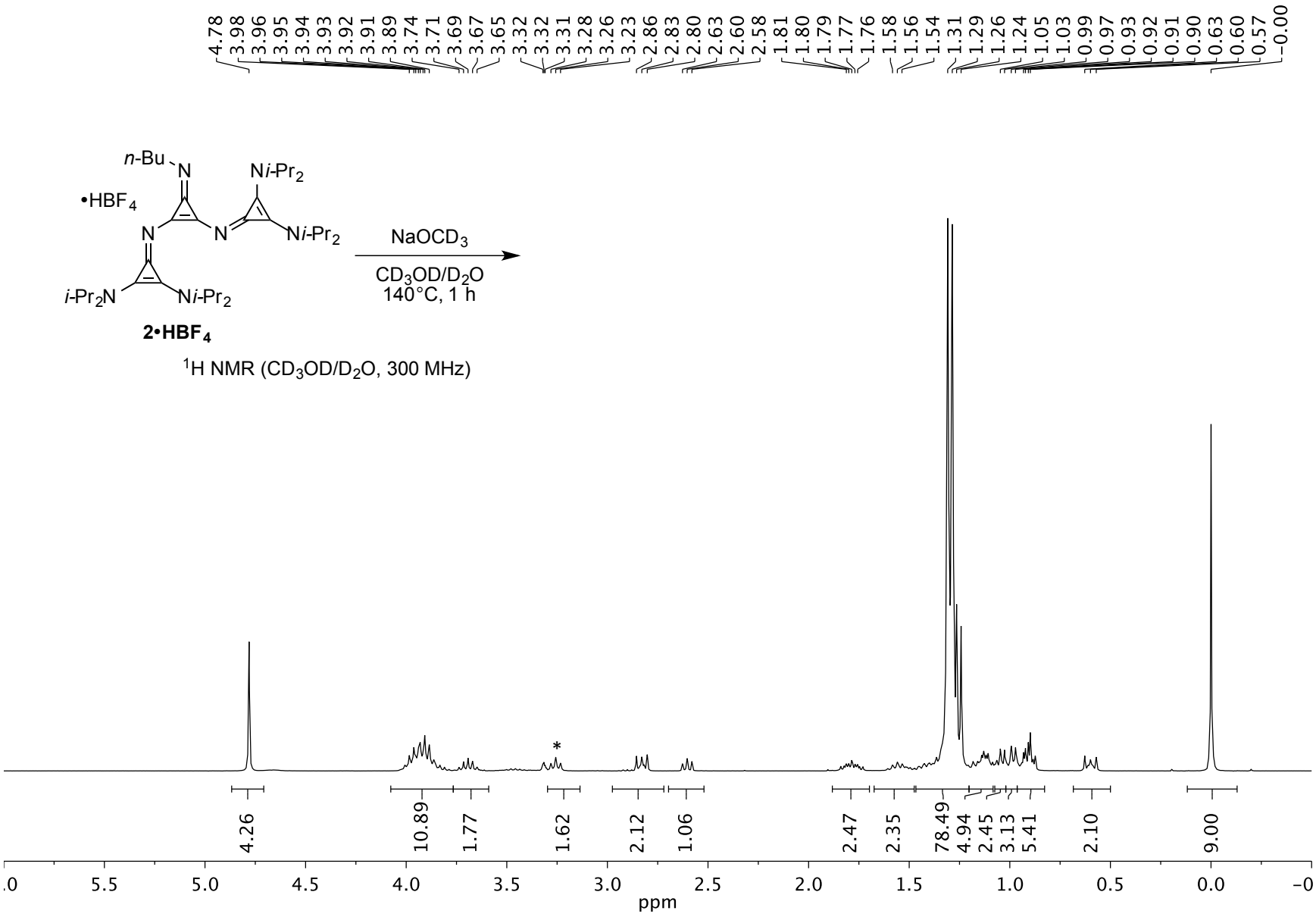

5.24
3.36
3.34
3.31
2.96
2.87
2.85
2.82
1.81
1.80
1.78
1.77
1.75
1.64
1.62
1.59
1.57
1.54
1.42
1.39
1.37
1.34
0.96
0.94
0.91
0.63
0.60
0.57
0.00
n-Bu
•HBF4
NMe2
NMe2
NMe2
Me2N
NMe2
NaOCD3
CD3OD/D2O, rt
4•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
*
6.05
4.22
41.87
10.97
2.36
2.04
3.57
3.64
5.31
2.02
9.00
ppm

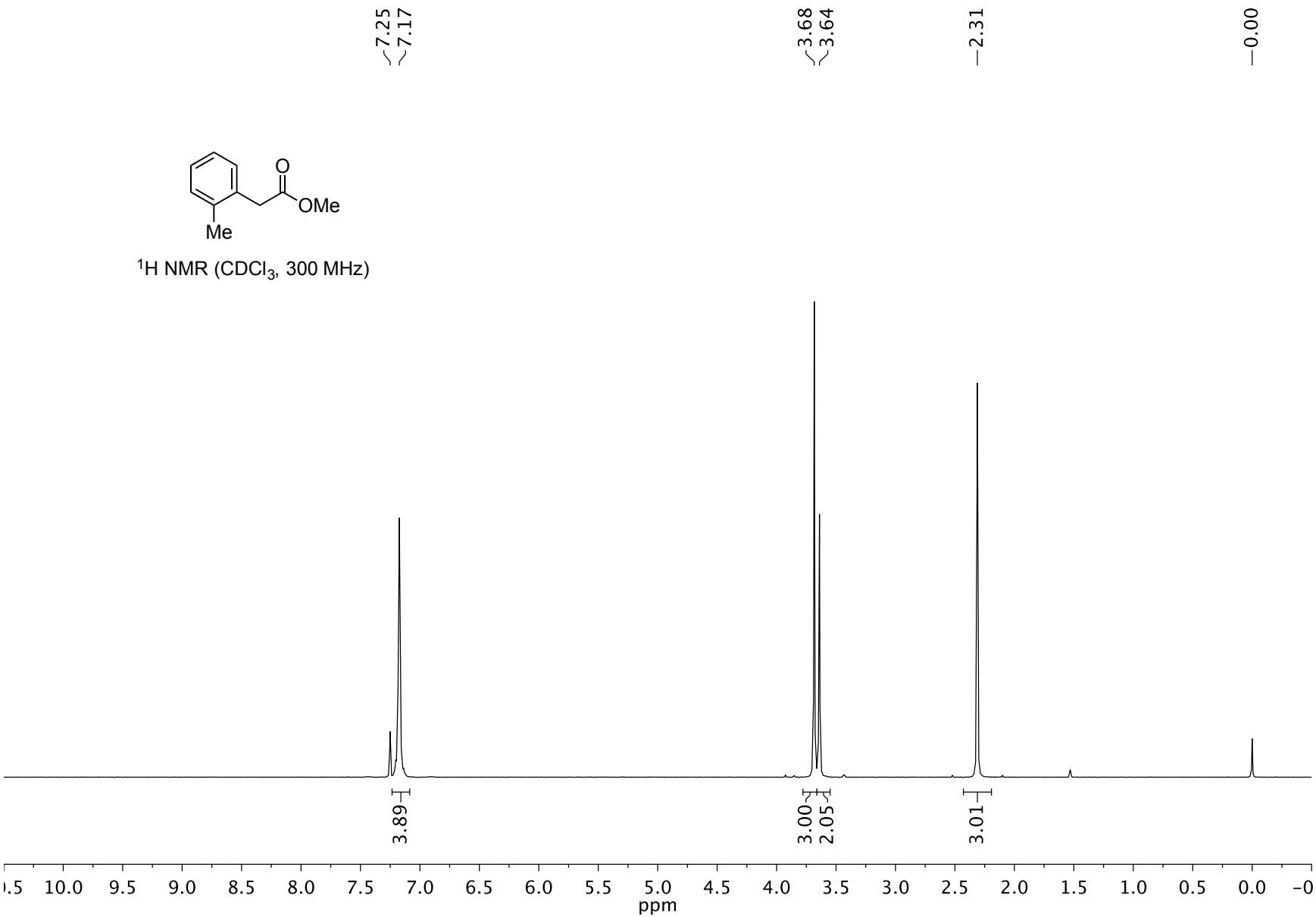

5.22
3.36
3.34
3.32
3.31
3.30
3.27
3.19
3.16
3.13
2.96
2.96
2.93
2.91
2.82
2.63
2.61
2.58
1.81
1.80
1.78
1.77
1.76
1.62
1.59
1.56
1.54
1.42
1.39
1.37
1.34
0.96
0.93
0.91
0.63
0.60
0.57
0.00
n-Bu
•HBF4
NMe2
NMe2
N
N
N
Me2N
NMe2
NaOCD3
CD3OD/D2O
80 °C, 15 min
4•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
*
6.22
3.65
5.44
32.22
6.17
0.49
4.24
2.04
3.08
4.02
5.26
2.02
9.00
ppm

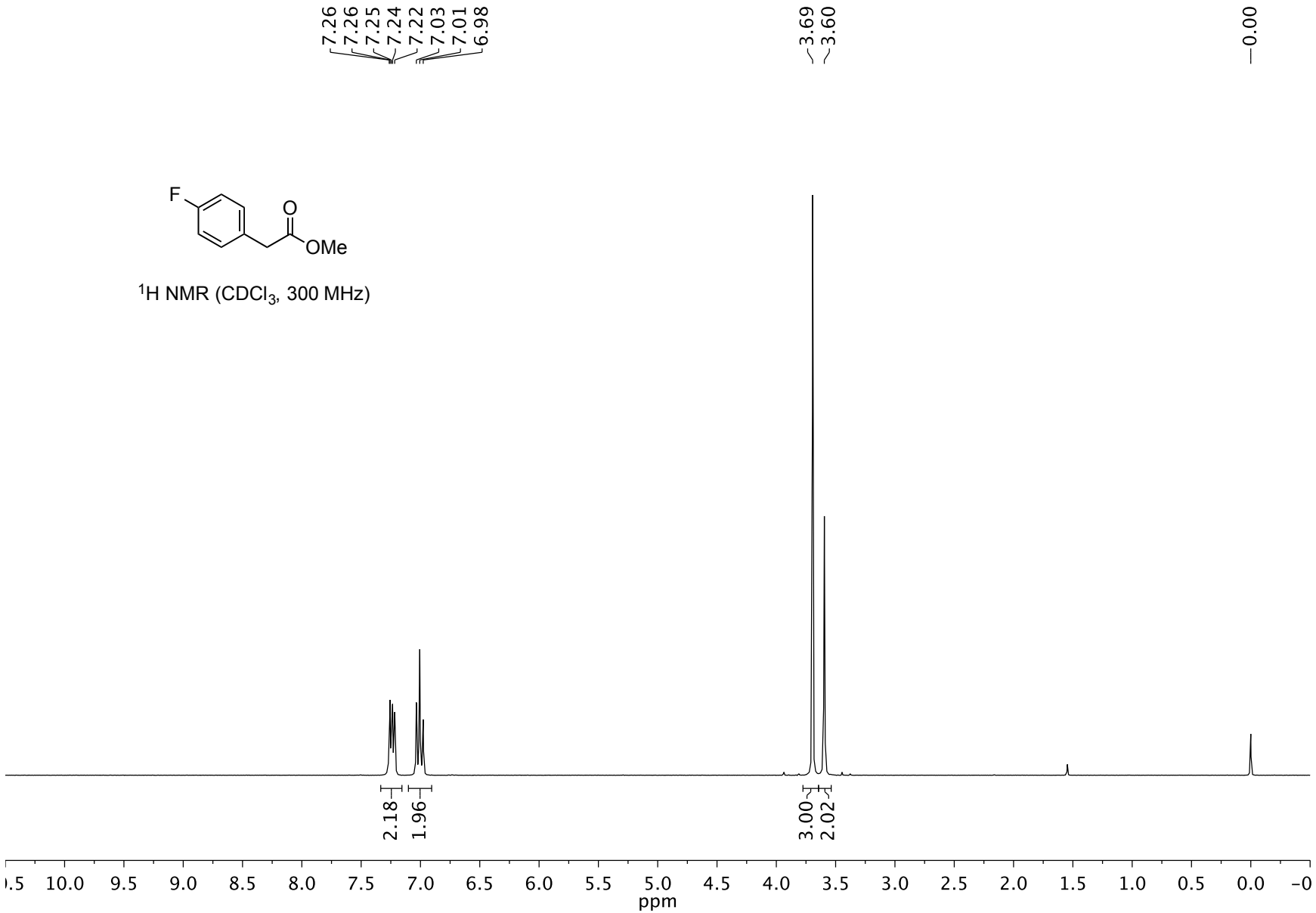

5.26
3.96
3.94
3.92
3.89
3.87
3.34
3.33
3.33
3.32
3.31
3.29
3.26
3.24
2.88
2.85
2.82
1.82
1.81
1.79
1.77
1.76
1.62
1.60
1.57
1.55
1.53
1.50
1.32
1.30
0.93
0.90
0.88
0.63
0.60
0.57
0.00
n-Bu
N
Ni-Pr2
•HBF4
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
NaOCD3
CD3OD/D2O, rt
2•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
4.09
13.58
3.28
2.00
2.10
4.16
85.04
5.16
2.04
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm

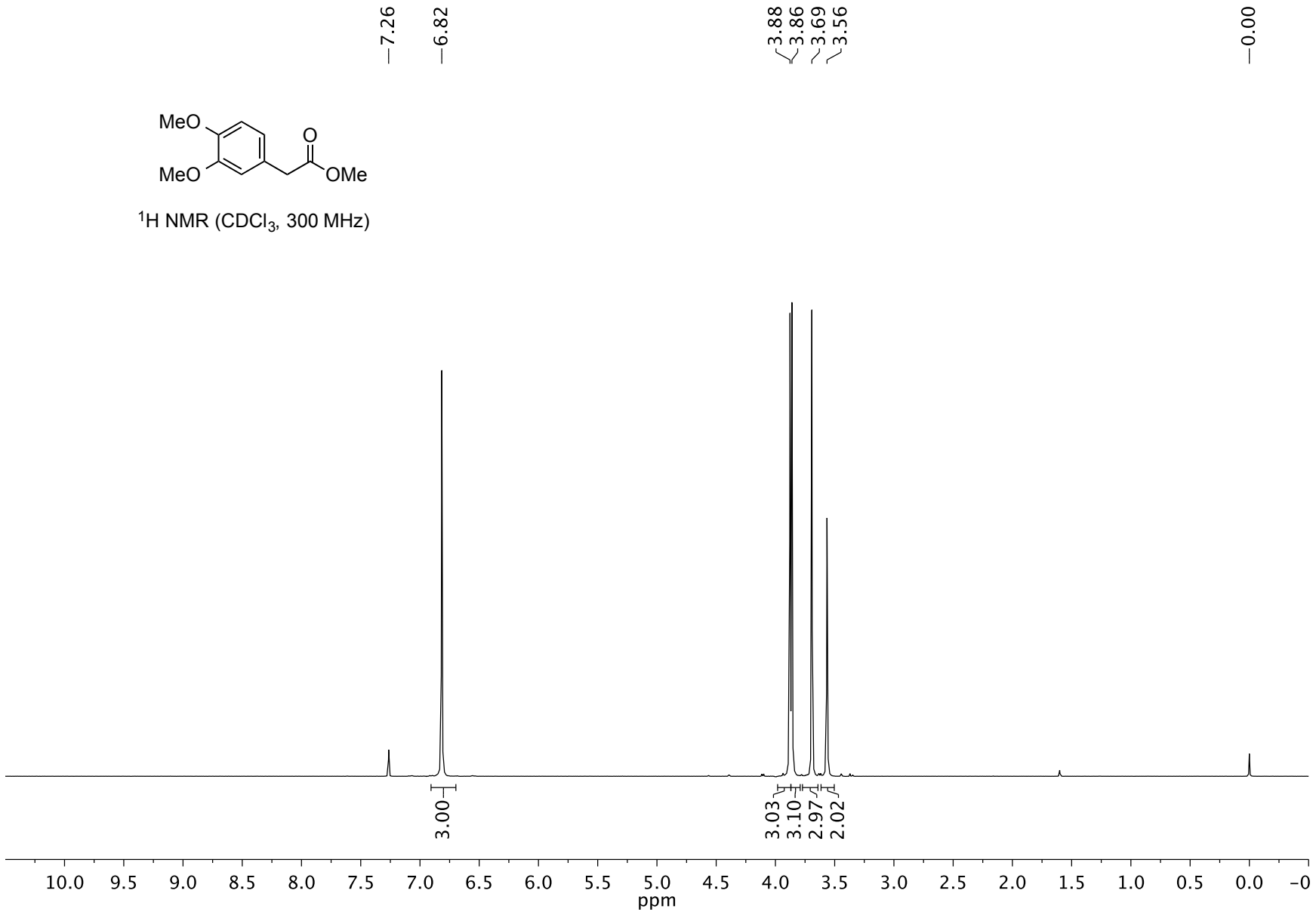

5.19
4.01
3.99
3.96
3.95
3.94
3.93
3.92
3.91
3.89
3.86
3.71
3.69
3.67
3.33
3.33
3.32
3.32
3.31
3.28
3.25
3.23
2.88
2.85
2.82
2.63
2.61
2.58
1.82
1.80
1.79
1.77
1.76
1.59
1.57
1.54
1.52
1.31
1.29
1.27
1.25
0.93
0.92
0.91
0.90
0.89
0.87
0.63
0.60
0.57
n-Bu
N
Ni-Pr2
•HBF4
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
NaOCD3
CD3OD/D2O
80°C, 9 h
2•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
4.08
12.18
1.02
1.65
2.08
1.35
2.28
2.55
83.91
4.85
2.03
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

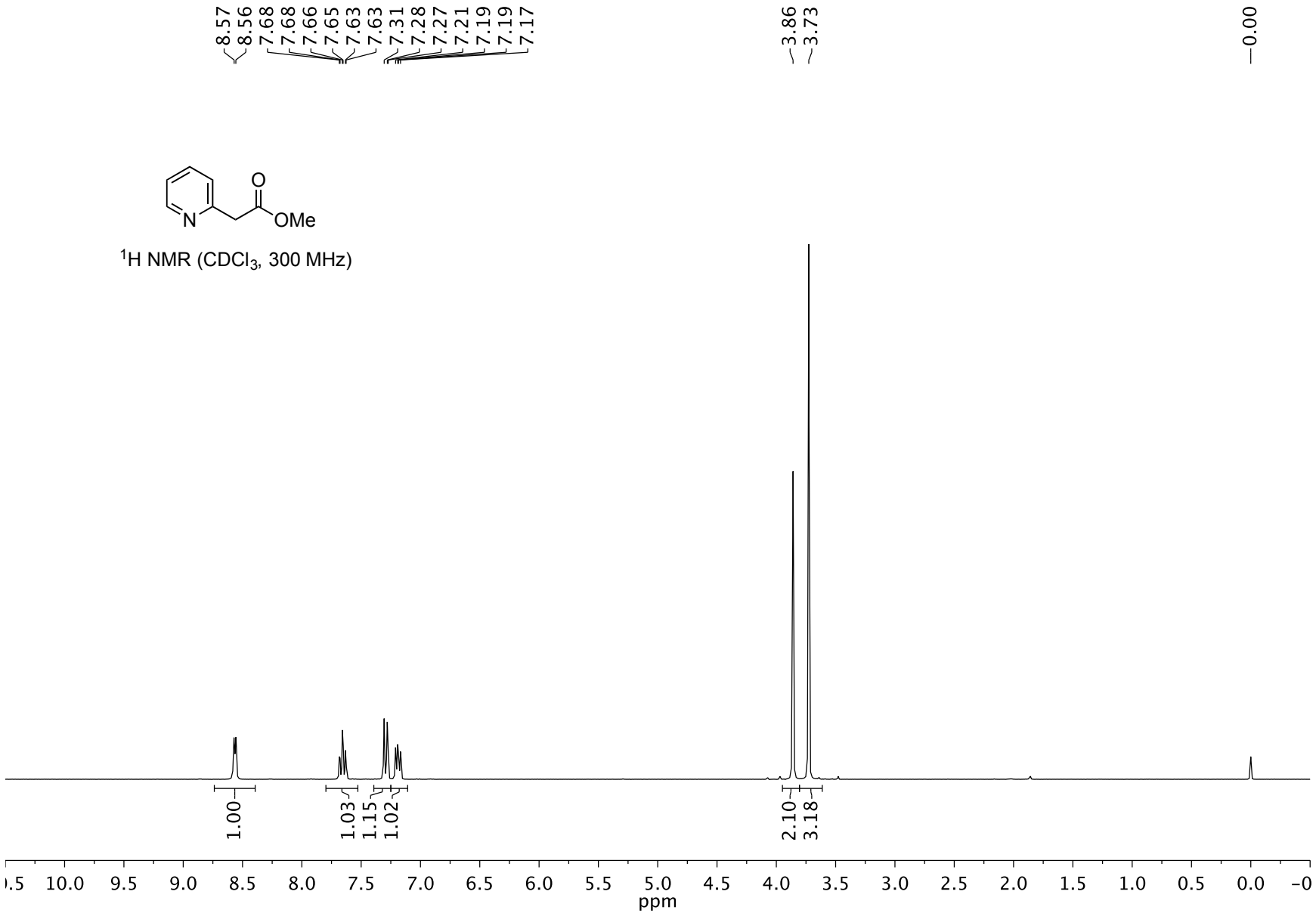

5.23
3.96
3.94
3.92
3.89
3.87
3.33
3.32
3.32
3.29
3.26
3.24
2.87
2.85
2.82
1.82
1.81
1.79
1.77
1.76
1.62
1.60
1.57
1.55
1.52
1.50
1.37
1.34
1.32
1.30
0.93
0.90
0.88
0.63
0.60
0.57
0.00
n-Bu
N
Ni-Pr2
•HBF4
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
NaOCD3
CD3OD/D2O, rt
2•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
*
3.73
13.76
3.31
1.98
2.06
4.10
87.15
5.31
2.03
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

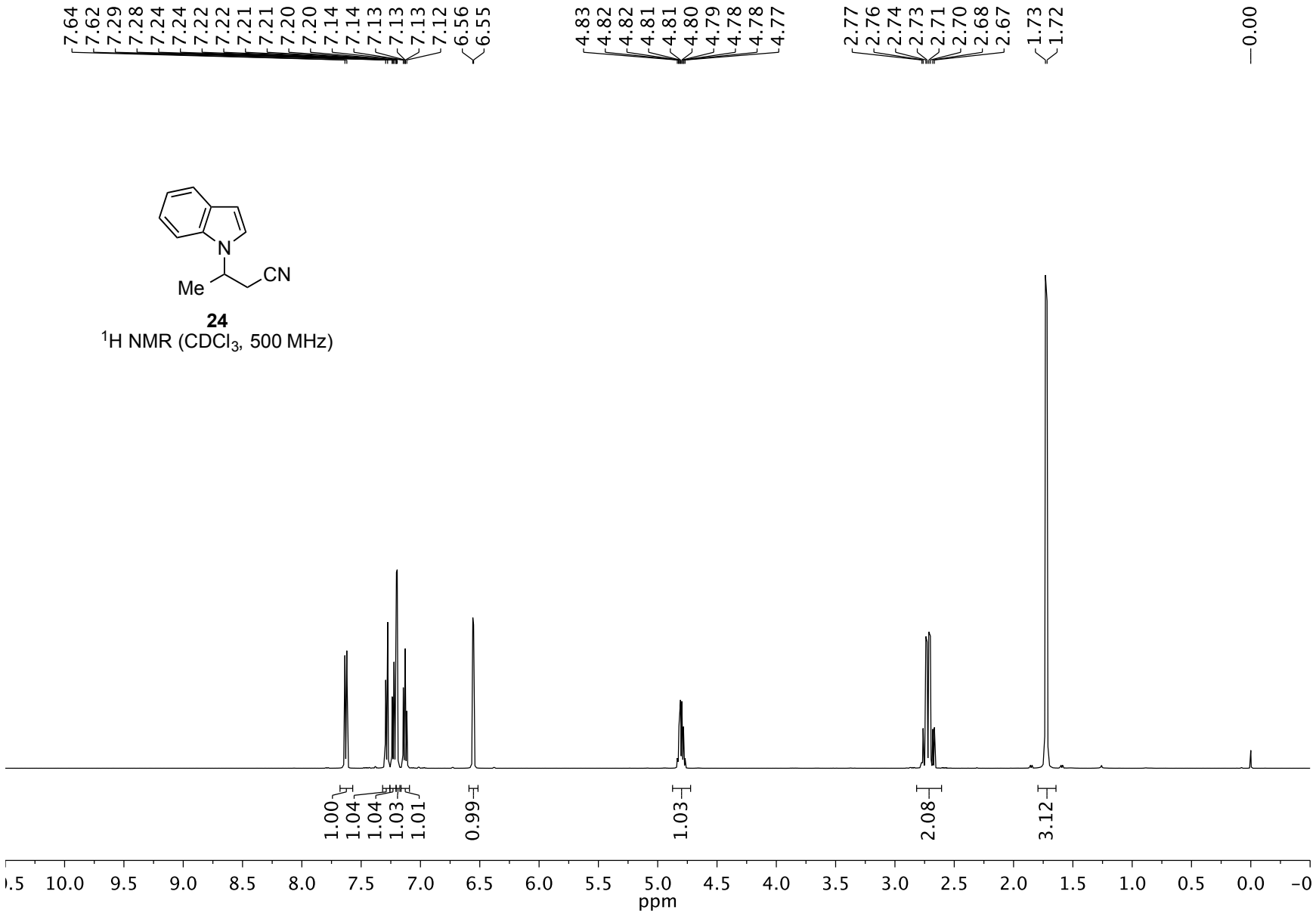

4.78
3.98
3.96
3.95
3.94
3.93
3.92
3.91
3.89
3.74
3.71
3.69
3.67
3.65
3.32
3.32
3.31
3.28
3.26
3.23
2.86
2.83
2.80
2.63
2.60
2.58
1.81
1.80
1.79
1.77
1.76
1.58
1.56
1.54
1.31
1.29
1.26
1.24
1.05
1.03
0.99
0.97
0.93
0.92
0.91
0.90
0.63
0.60
0.57
-0.00
n-Bu
N
Ni-Pr2
•HBF4
N
N
Ni-Pr2
i-Pr2N
Ni-Pr2
NaOCD3
CD3OD/D2O
140°C, 1 h
2•HBF4
1H NMR (CD3OD/D2O, 300 MHz)
*
4.26
10.89
1.77
1.62
2.12
1.06
2.47
2.35
78.49
4.94
2.45
3.13
5.41
2.10
9.00
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


7.25
7.17
3.68
3.64
2.31
0.00
O
OMe
Me
1H NMR (CDCl3, 300 MHz)
3.89
3.00
2.05
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


7.26
7.26
7.25
7.24
7.22
7.03
7.01
6.98
3.69
3.60
0.00
F
O
OMe
1H NMR (CDCl3, 300 MHz)
2.18
1.96
3.00
2.02
ppm

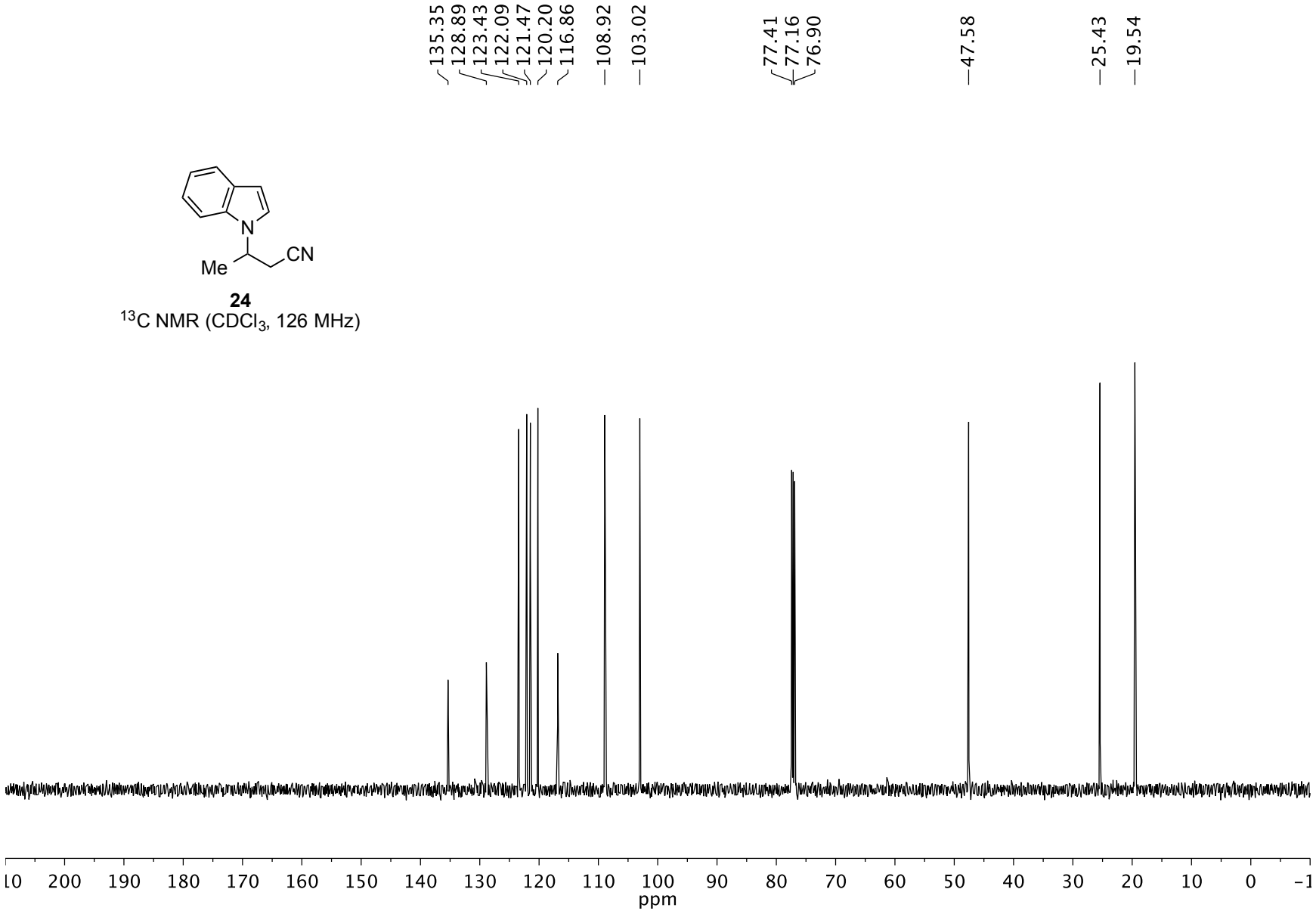

7.26
6.82
3.88
3.86
3.69
3.56
0.00
MeO
MeO
O
OMe
1H NMR (CDCl3, 300 MHz)
3.00
3.03
3.10
2.97
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
ppm


8.57
8.56
7.68
7.68
7.66
7.65
7.63
7.63
7.31
7.28
7.27
7.21
7.19
7.19
7.17
3.86
3.73
0.00
O
N
OMe
1H NMR (CDCl3, 300 MHz)
1.00
1.03
1.15
1.02
2.10
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



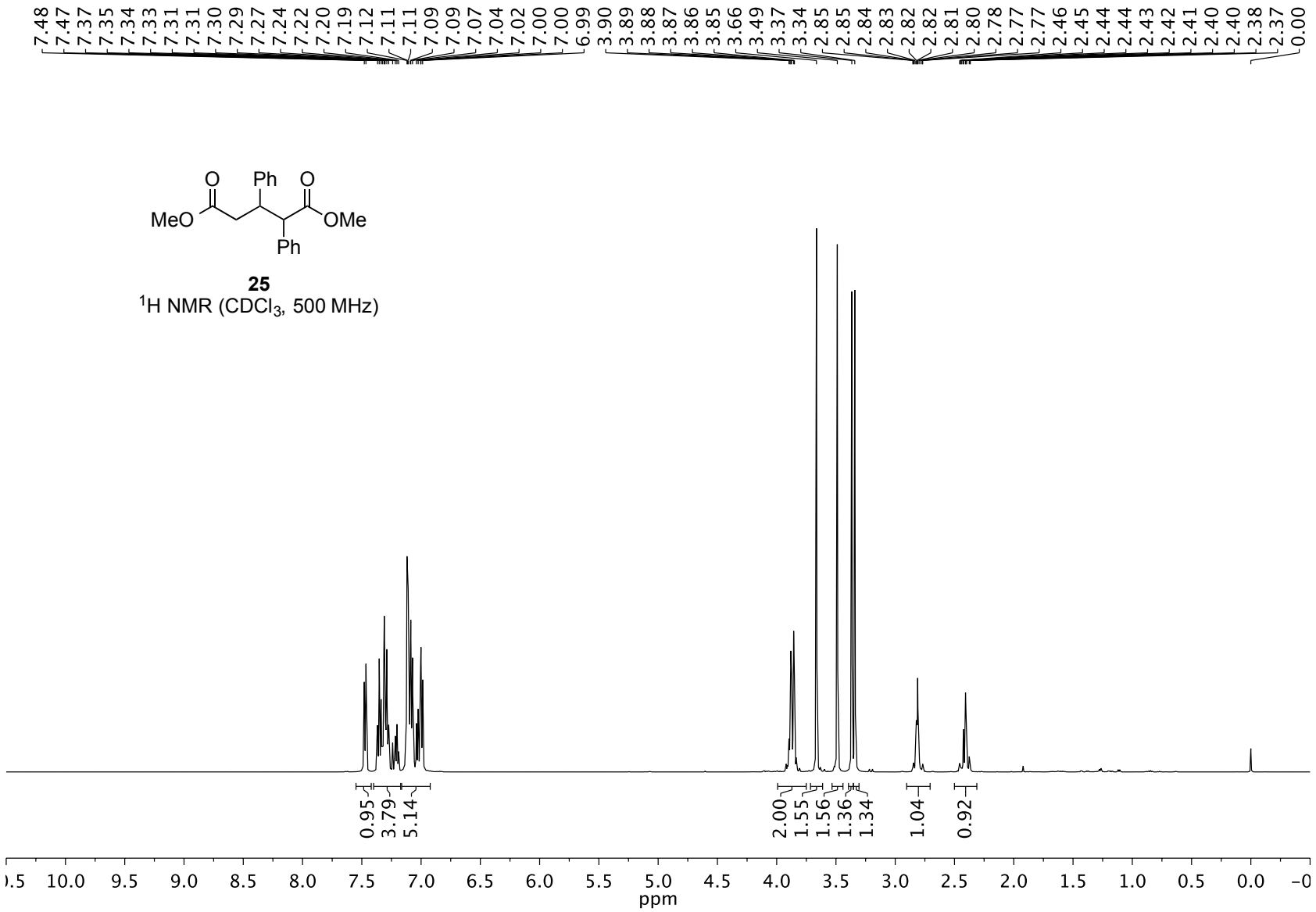
24

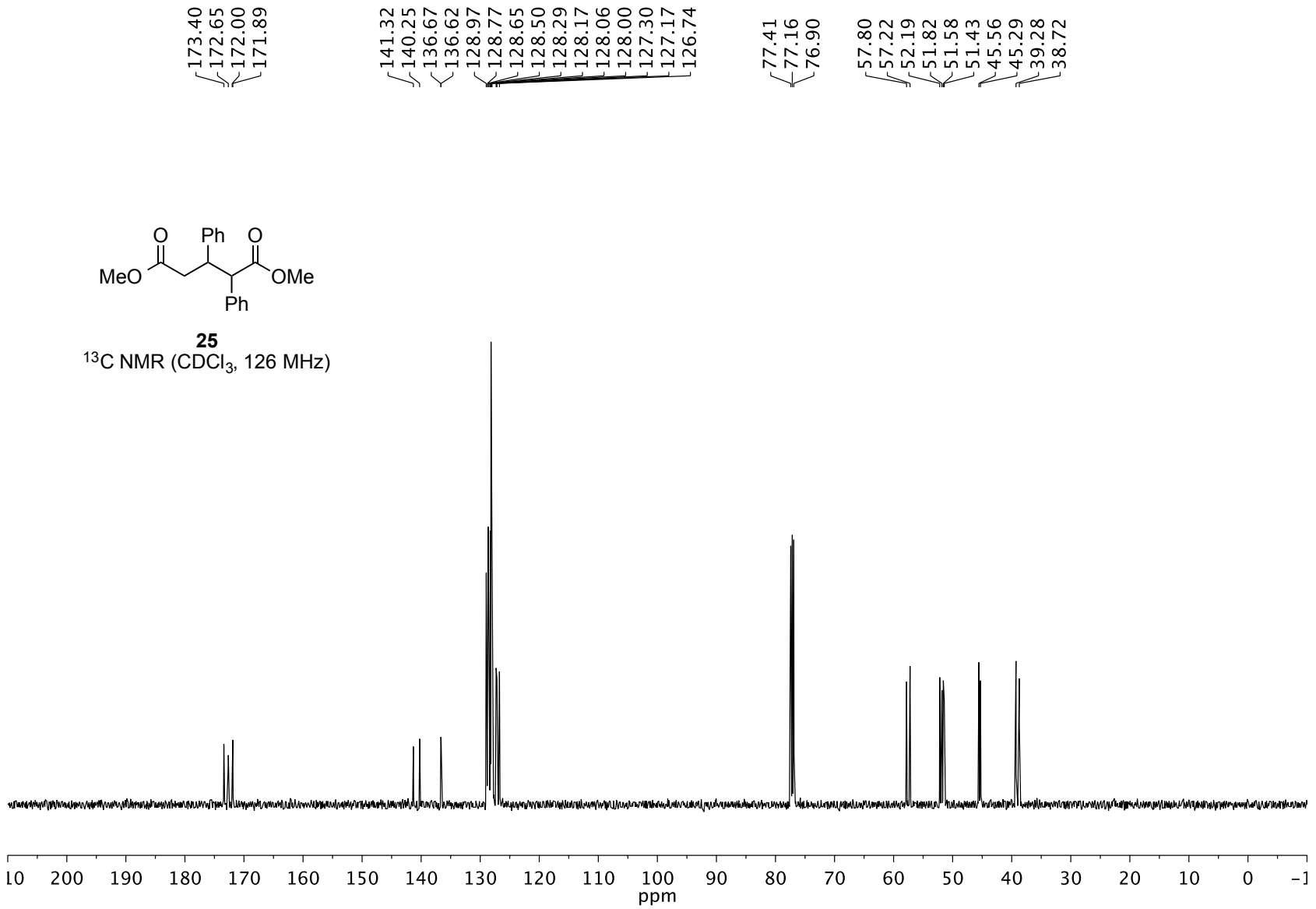
^{1}H NMR ($CDCl_3$, 500 MHz)



24

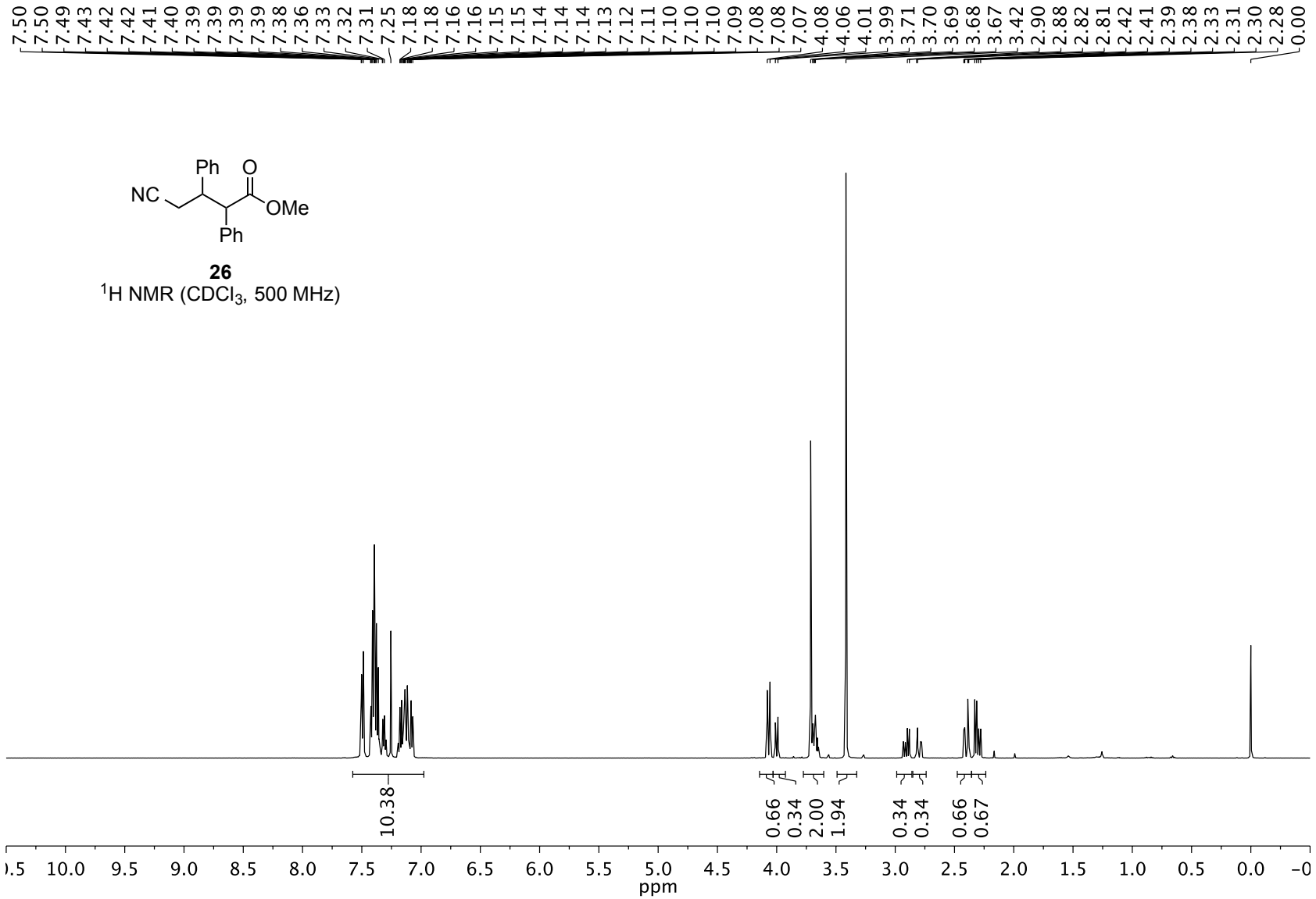
^{13}C NMR ($CDCl_3$, 126 MHz)


7.48 7.47 7.37 7.35 7.34 7.33 7.31 7.31 7.30 7.29 7.27 7.24 7.22 7.20 7.19 7.12 7.11 7.11 7.09 7.09 7.07 7.04 7.02 7.00 7.00 6.99
3.90 3.89 3.88 3.87 3.86 3.85 3.66 3.49 3.37 3.34 2.85 2.85 2.84 2.83 2.82 2.82 2.81 2.80 2.78 2.77 2.77 2.46 2.45 2.44 2.44 2.43 2.42 2.41 2.40 2.40 2.38 2.37 0.00
O
Ph
O
MeO
OMe
Ph
25
1H NMR (CDCl3, 500 MHz)
0.95
3.79
5.14
2.00
1.55
1.56
1.36
1.34
1.04
0.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm



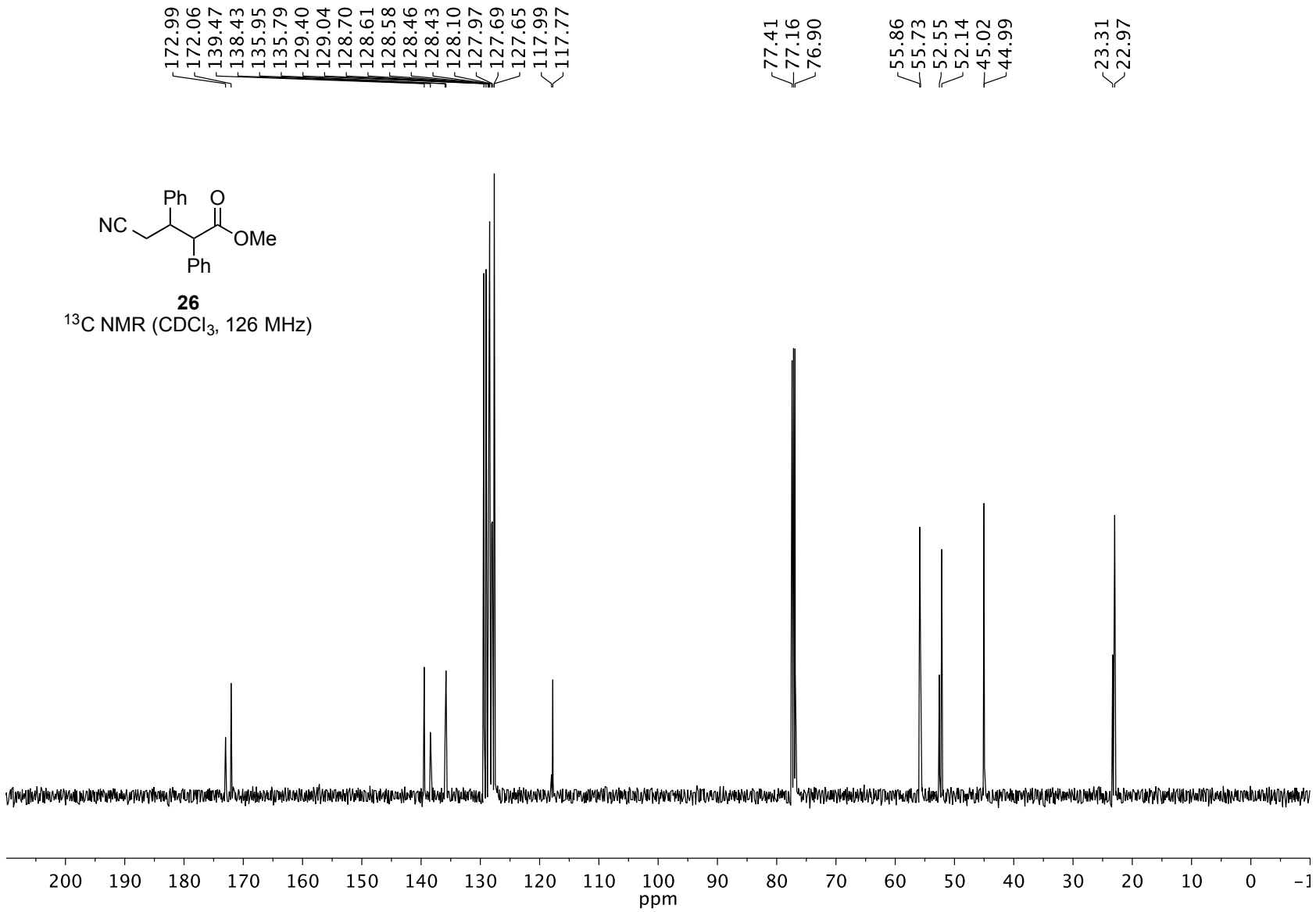
25

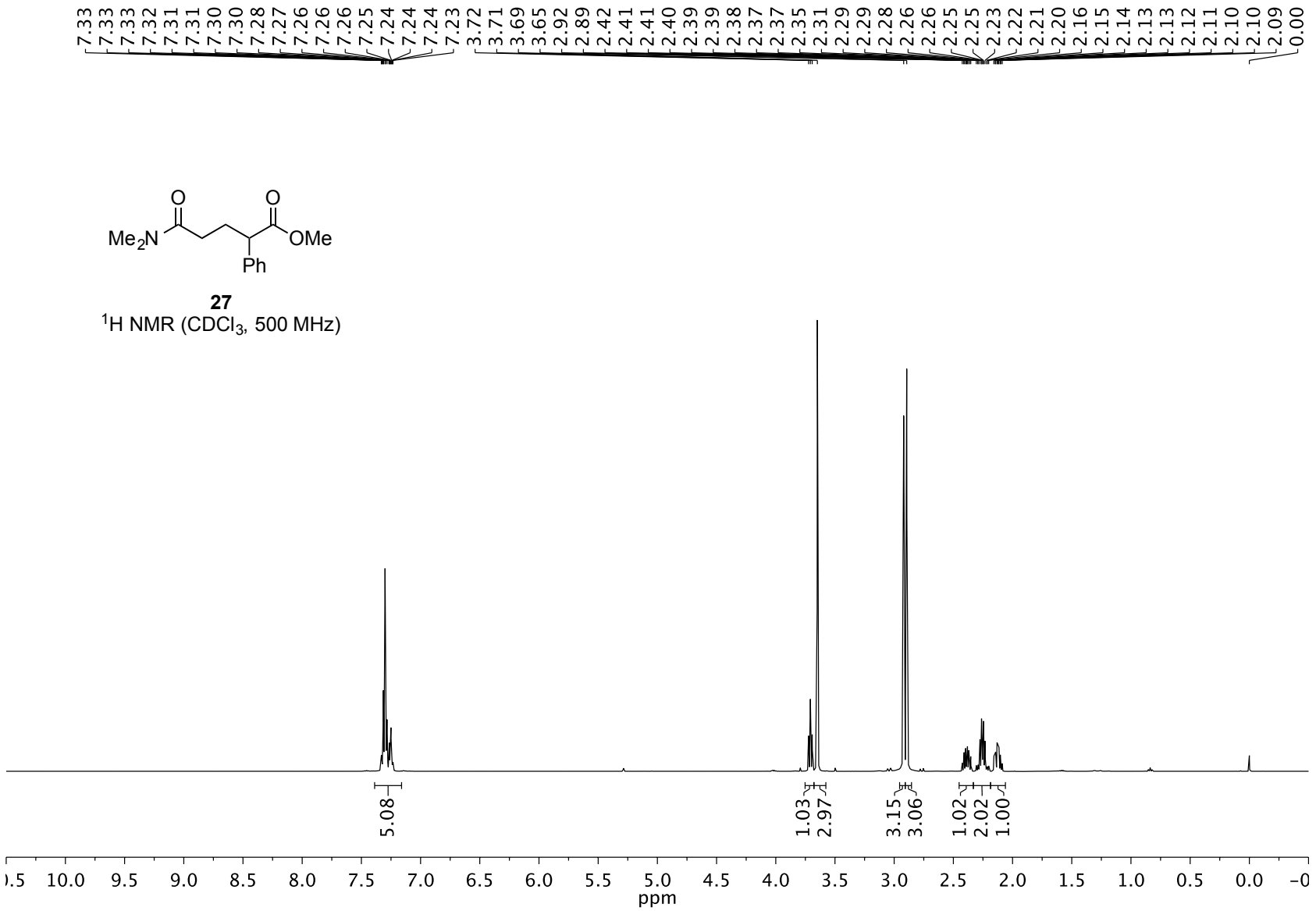
^{13}C NMR ($CDCl_3$, 126 MHz)

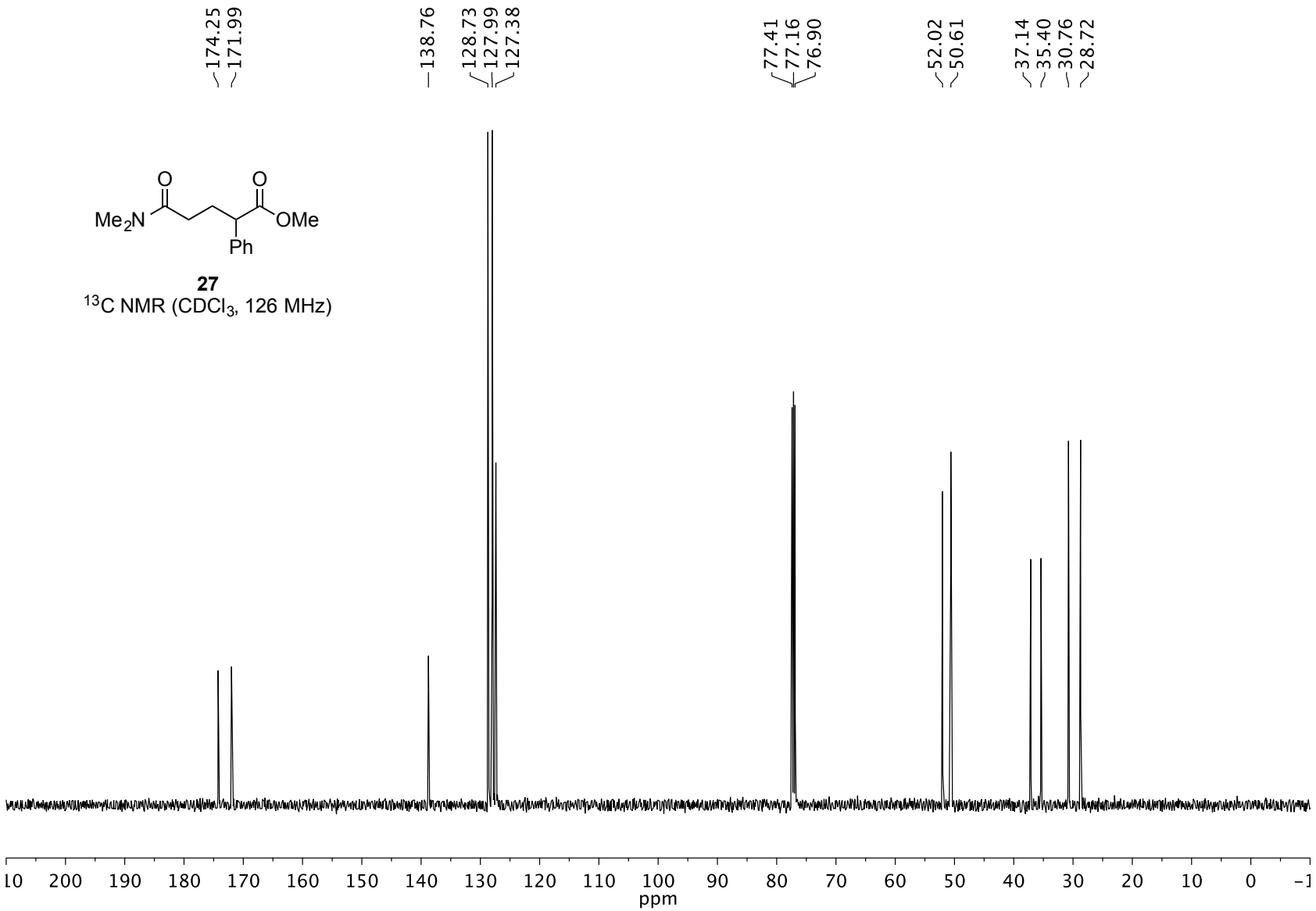


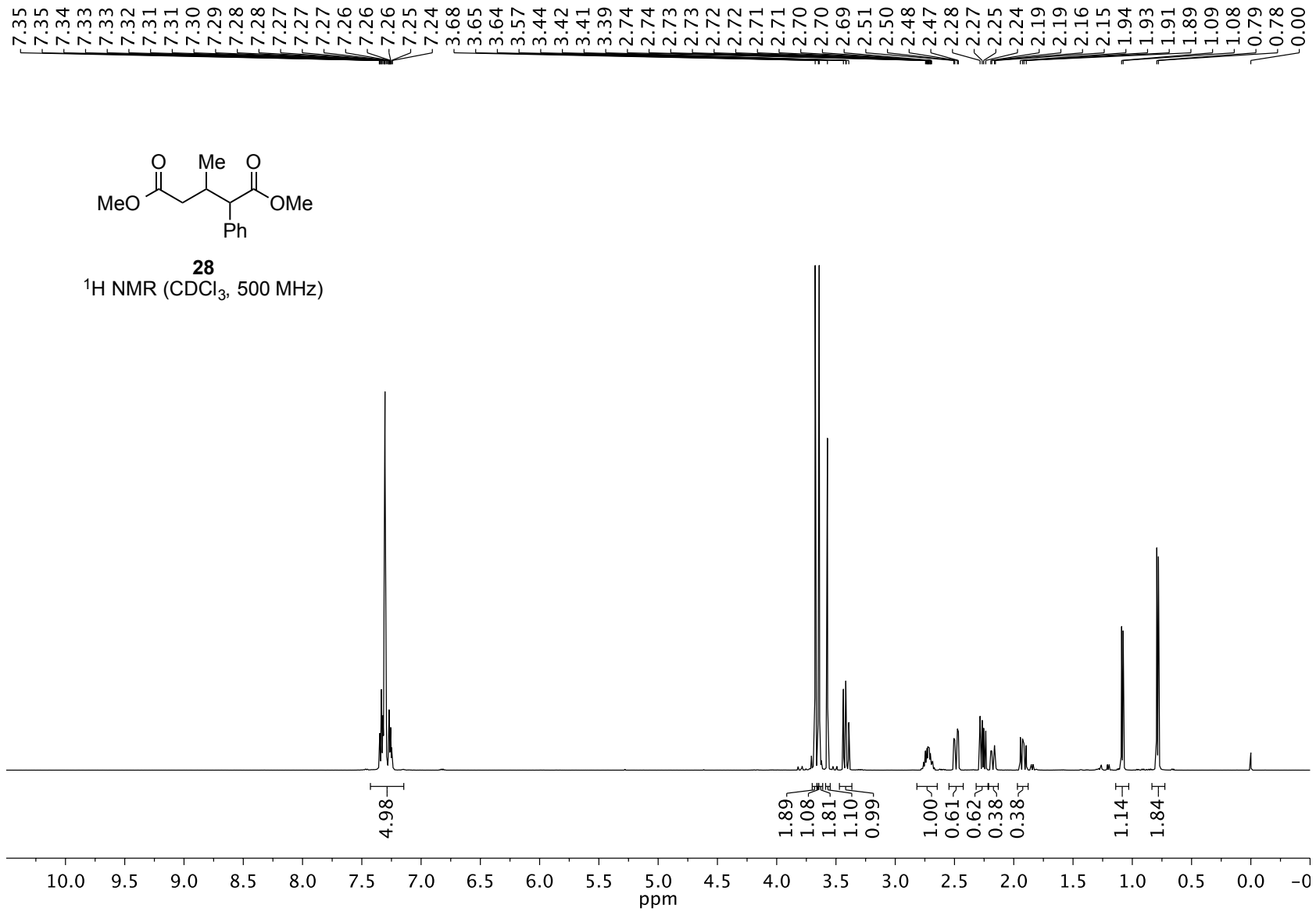
26

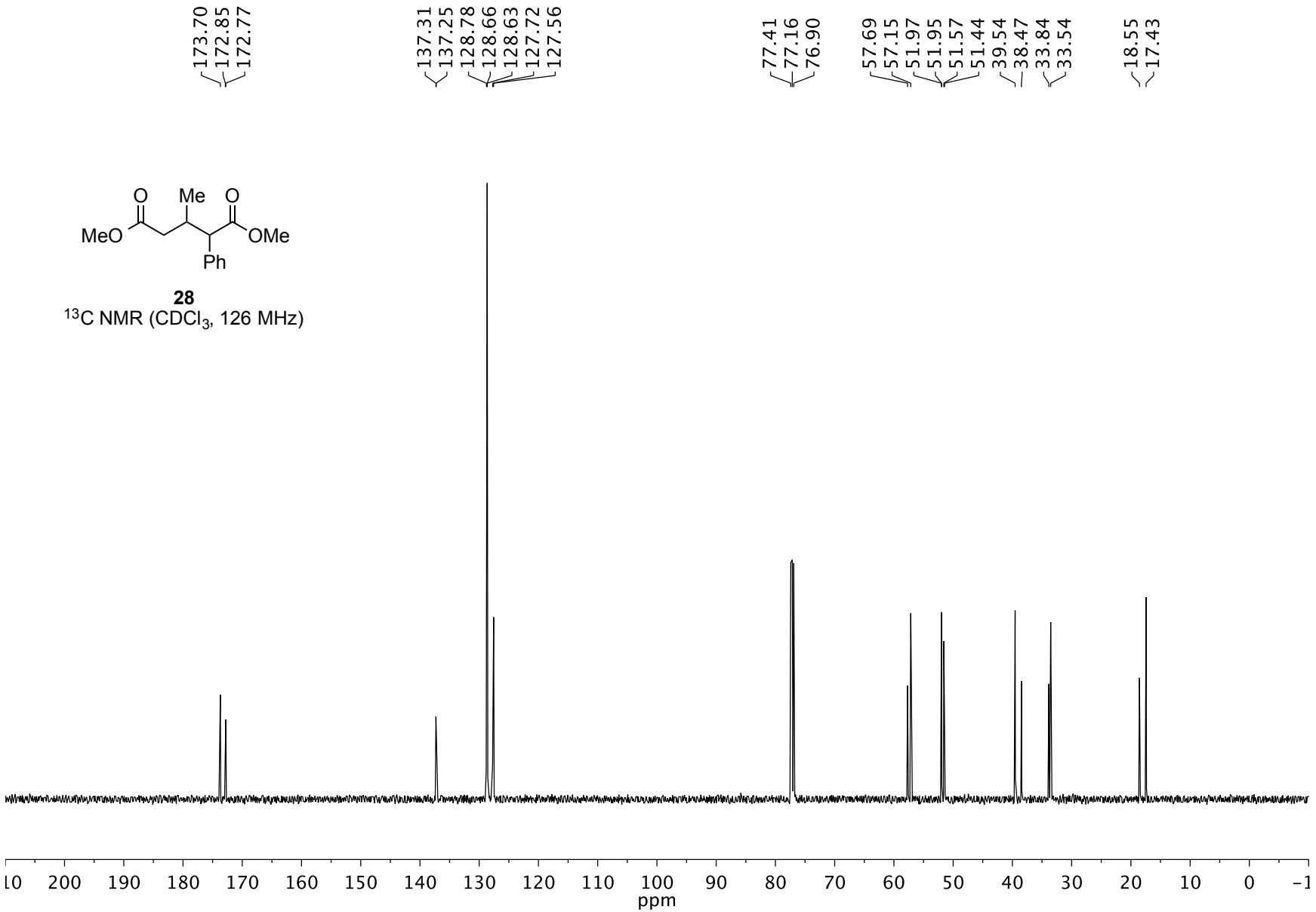
^{1}H NMR ($CDCl_3$, 500 MHz)


172.99
172.06
139.47
138.43
135.95
135.79
129.40
129.04
128.70
128.61
128.58
128.46
128.43
128.10
127.97
127.69
127.65
117.99
117.77
77.41
77.16
76.90
55.86
55.73
52.55
52.14
45.02
44.99
23.31
22.97
Ph
O
NC
OMe
Ph
26
13C NMR (CDCl3, 126 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.28 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.23
3.72 3.71 3.69 3.65 2.92 2.89 2.42 2.41 2.41 2.40 2.39 2.39 2.38 2.37 2.37 2.35 2.31 2.29 2.29 2.28 2.26 2.26 2.25 2.25 2.23 2.22 2.21 2.20 2.16 2.15 2.14 2.13 2.13 2.12 2.11 2.10 2.10 2.09 0.00
O
O
Me2N
OMe
Ph
27
1H NMR (CDCl3, 500 MHz)
5.08
1.03
2.97
3.15
3.06
1.02
2.02
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

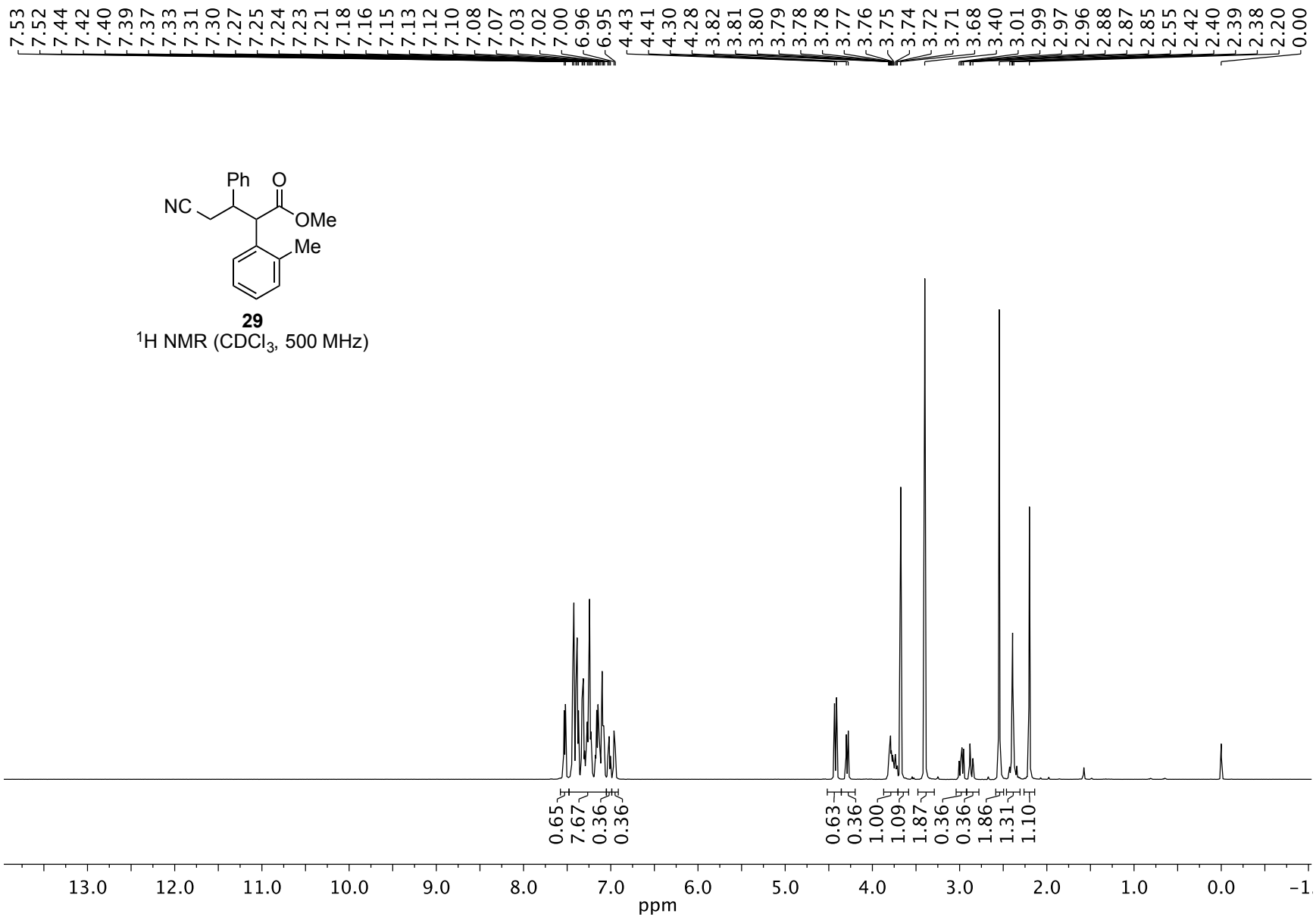

174.25
171.99
138.76
128.73
127.99
127.38
77.41
77.16
76.90
52.02
50.61
37.14
35.40
30.76
28.72
O
O
Me2N
OMe
Ph
27
13C NMR (CDCl3, 126 MHz)
ppm


7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.24
3.68 3.65 3.64 3.57 3.44 3.42 3.41 3.39 2.74 2.74 2.73 2.73 2.72 2.72 2.71 2.71 2.70 2.70 2.69 2.51 2.50 2.48 2.47 2.28 2.27 2.25 2.24 2.19 2.19 2.16 2.15 1.94 1.93 1.91 1.89 1.09 1.08 0.79 0.78 0.00
O
Me
O
MeO
OMe
Ph
28
1H NMR (CDCl3, 500 MHz)
4.98
1.89
1.08
1.81
1.10
0.99
1.00
0.61
0.62
0.38
0.38
1.14
1.84
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
ppm



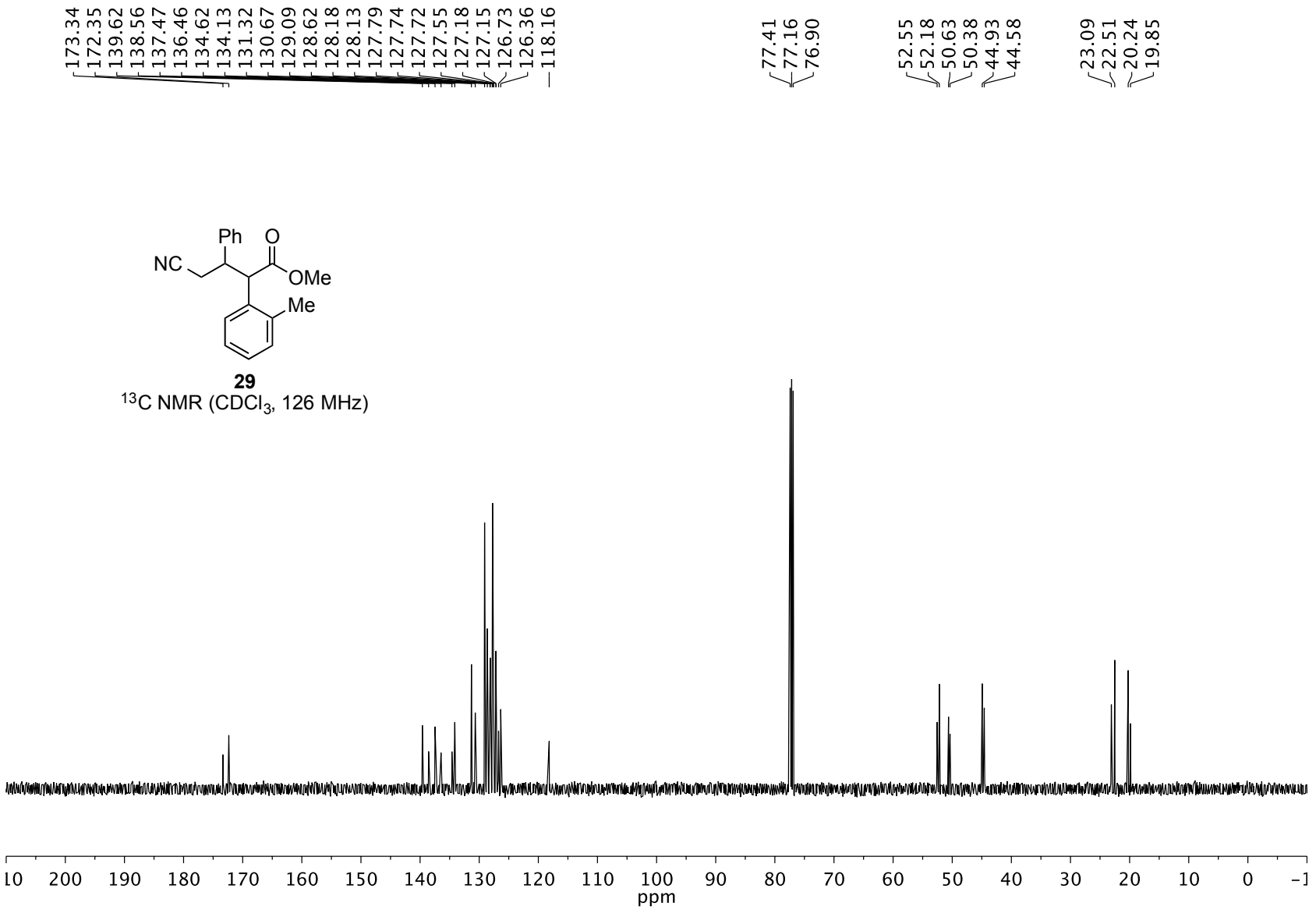
28

^{13}C NMR ($CDCl_3$, 126 MHz)



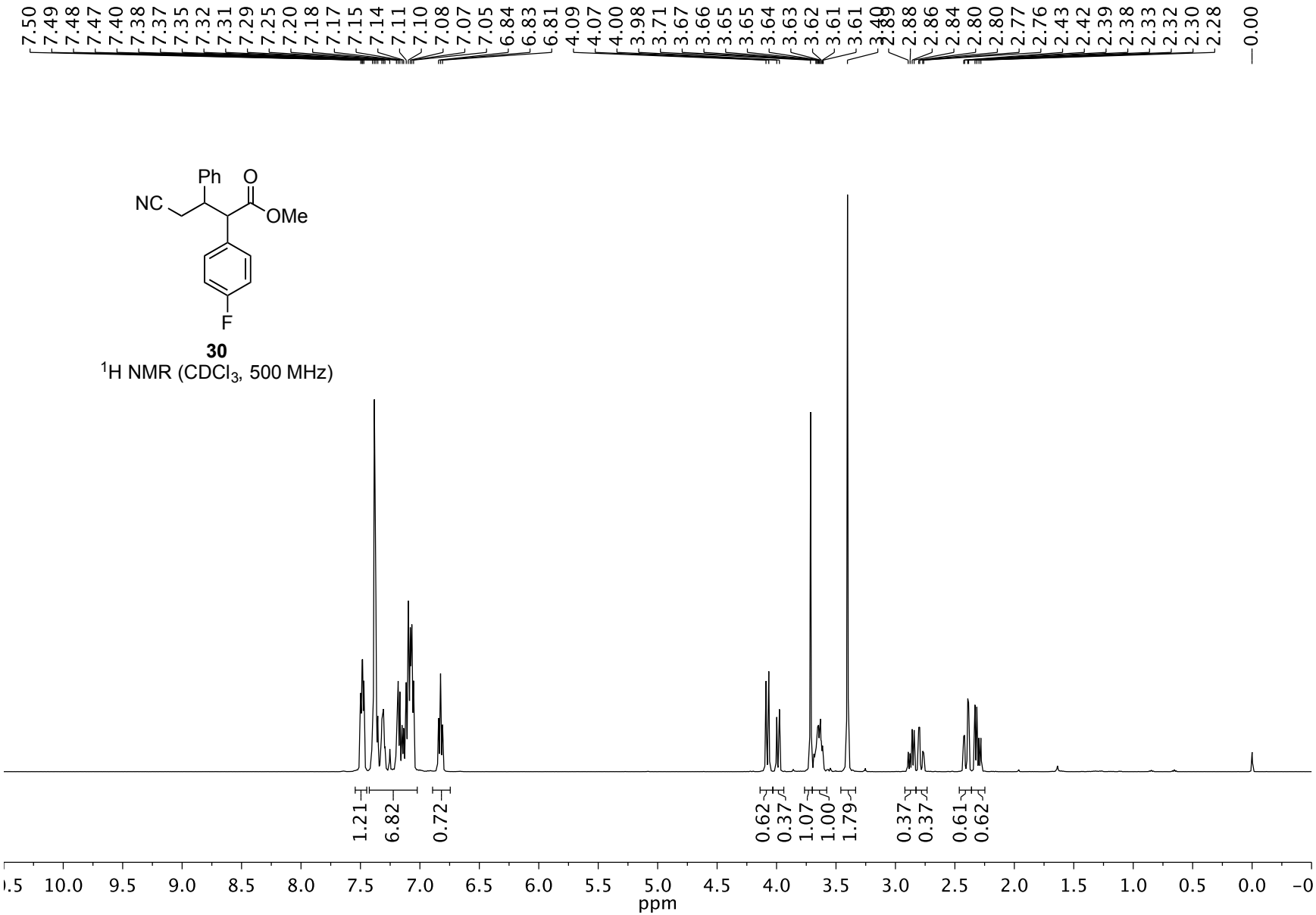
29

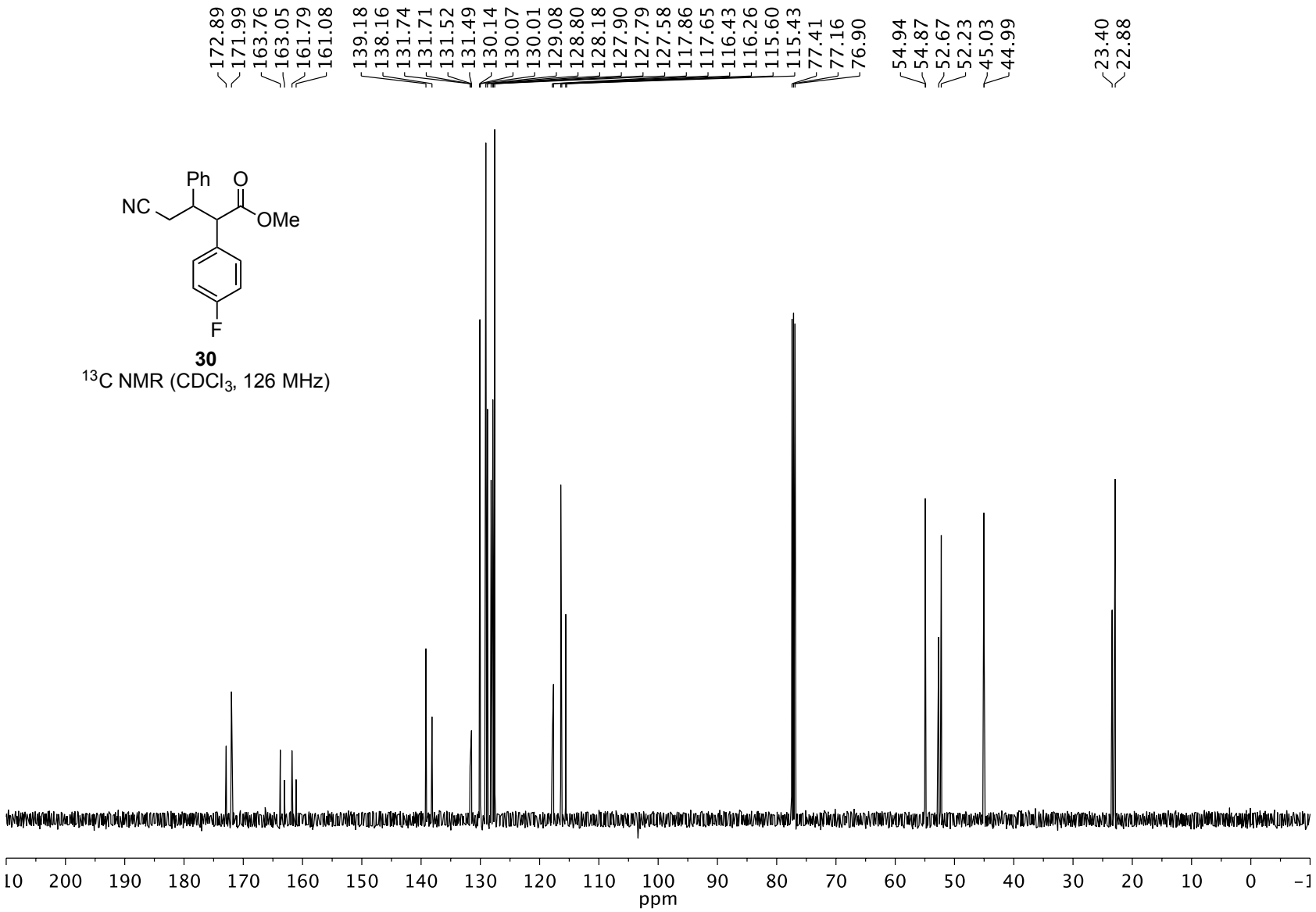
^{1}H NMR ($CDCl_3$, 500 MHz)



29

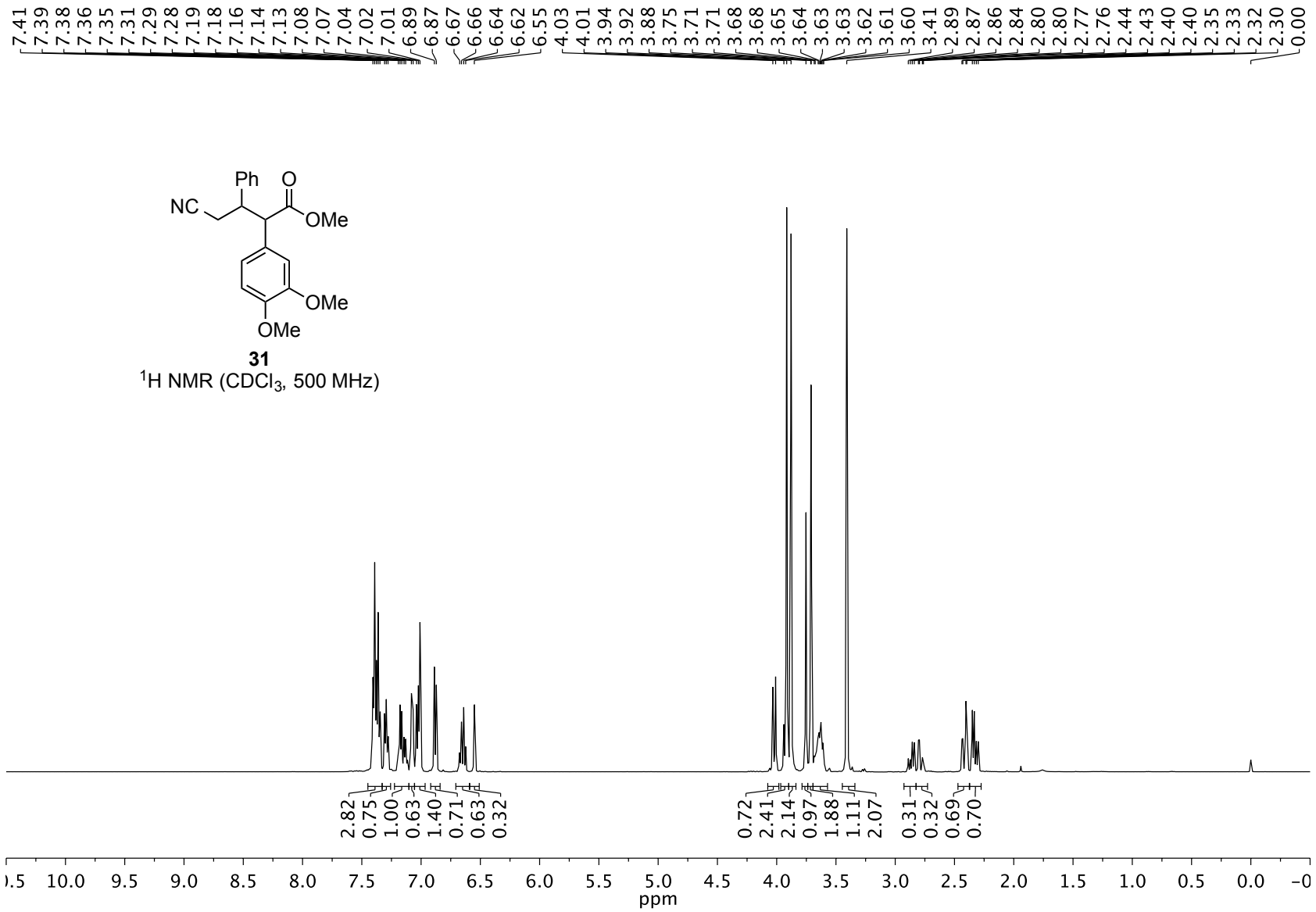
^{13}C NMR ($CDCl_3$, 126 MHz)


7.50 7.49 7.48 7.47 7.40 7.38 7.37 7.35 7.32 7.31 7.29 7.25 7.20 7.18 7.17 7.15 7.14 7.11 7.10 7.08 7.07 7.05 6.84 6.83 6.81
4.09 4.07 4.00 3.98 3.71 3.67 3.66 3.65 3.65 3.64 3.63 3.62 3.61 3.61 3.40 2.89 2.88 2.86 2.84 2.80 2.80 2.77 2.76 2.43 2.42 2.39 2.38 2.33 2.32 2.30 2.28
0.00
Ph
O
NC
OMe
F
30
1H NMR (CDCl3, 500 MHz)
1.21
6.82
0.72
0.62
0.37
1.07
1.00
1.79
0.37
0.37
0.61
0.62
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm



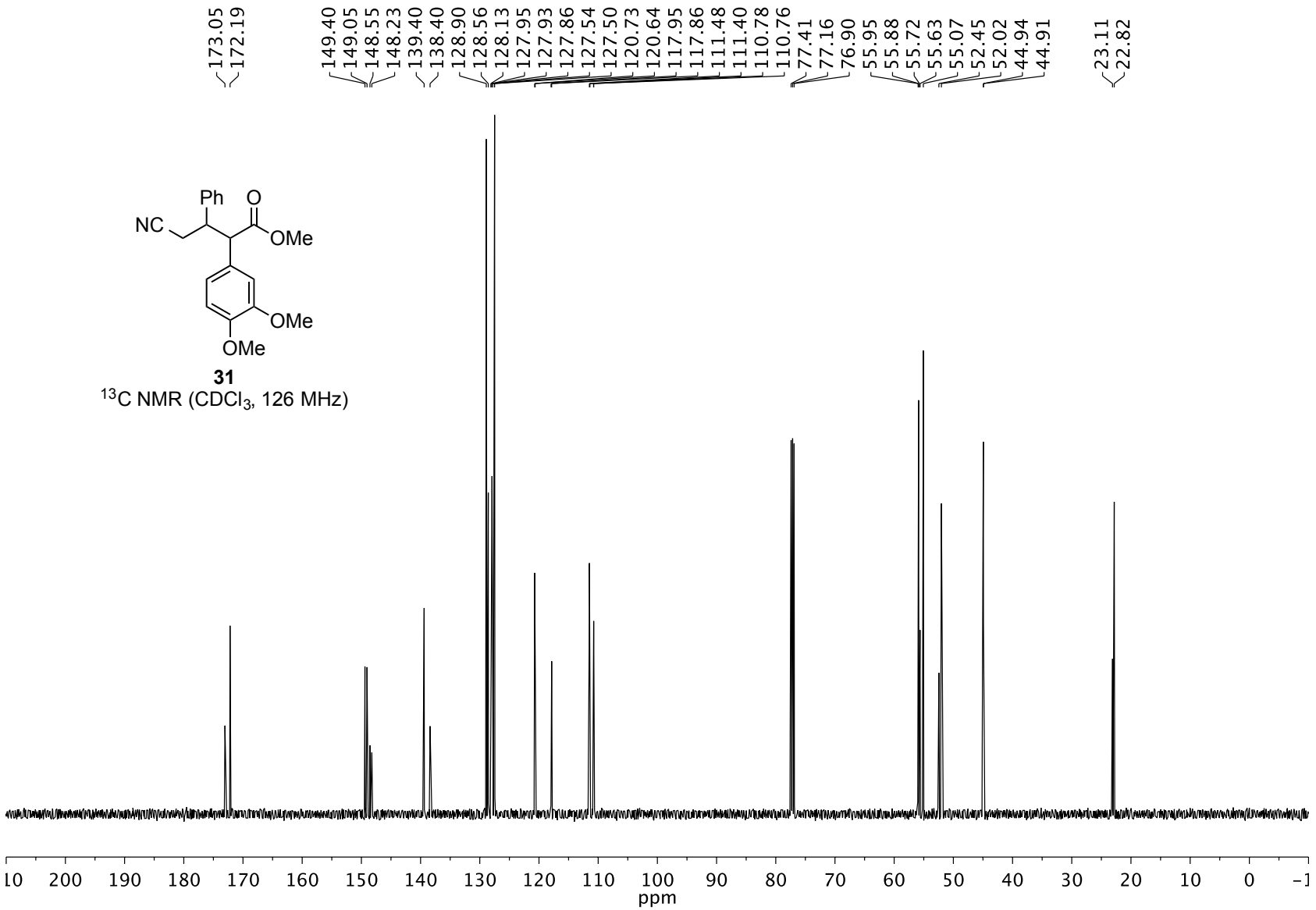
30

^{13}C NMR ($CDCl_3$, 126 MHz)



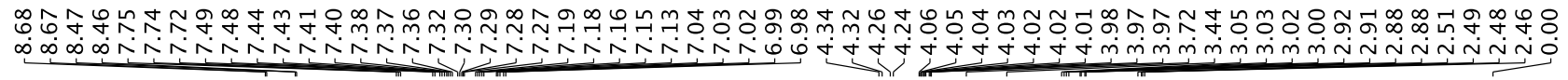
31

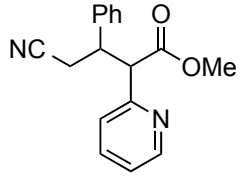
^{1}H NMR ($CDCl_3$, 500 MHz)



31

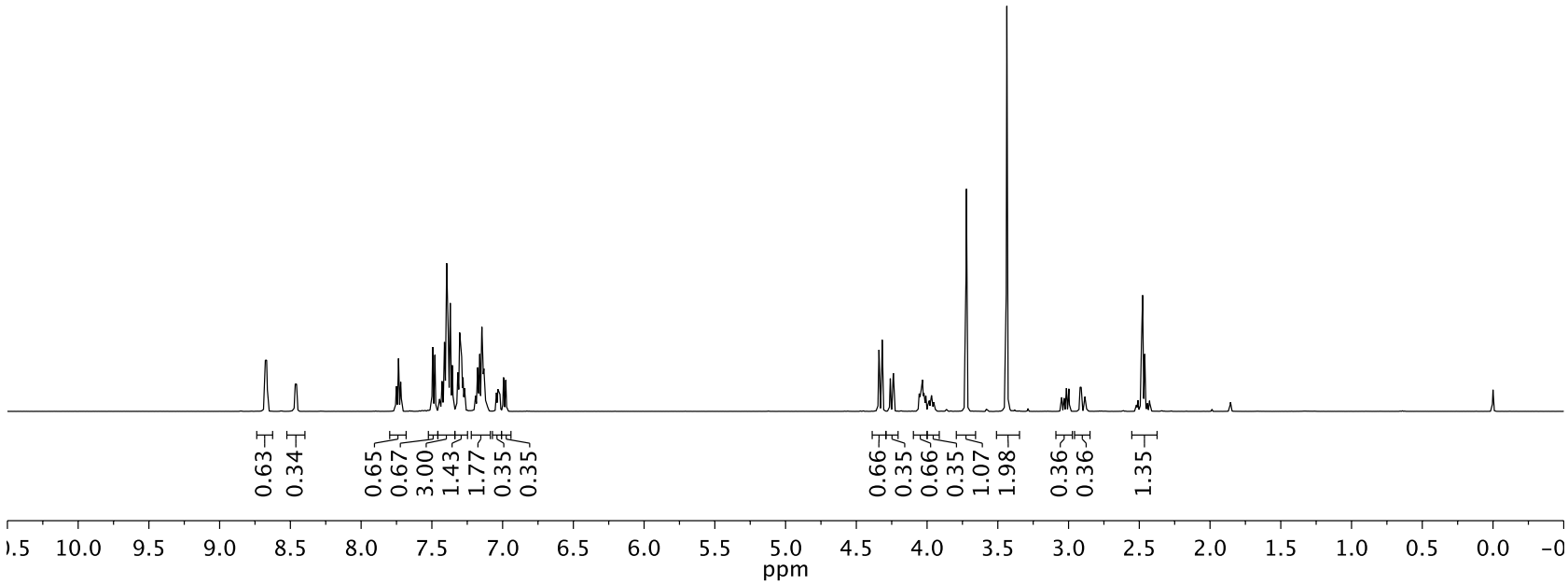
^{13}C NMR ($CDCl_3$, 126 MHz)

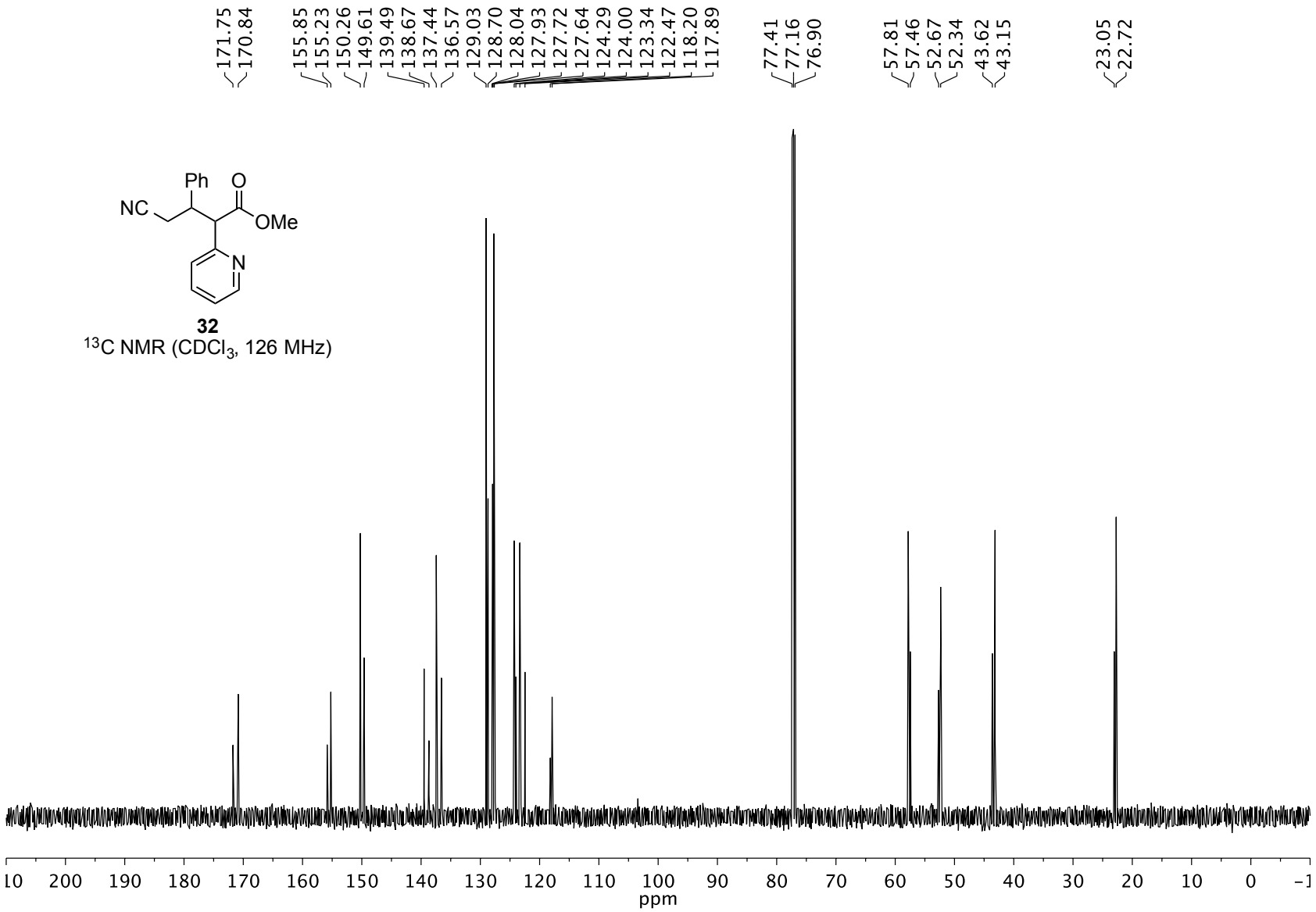


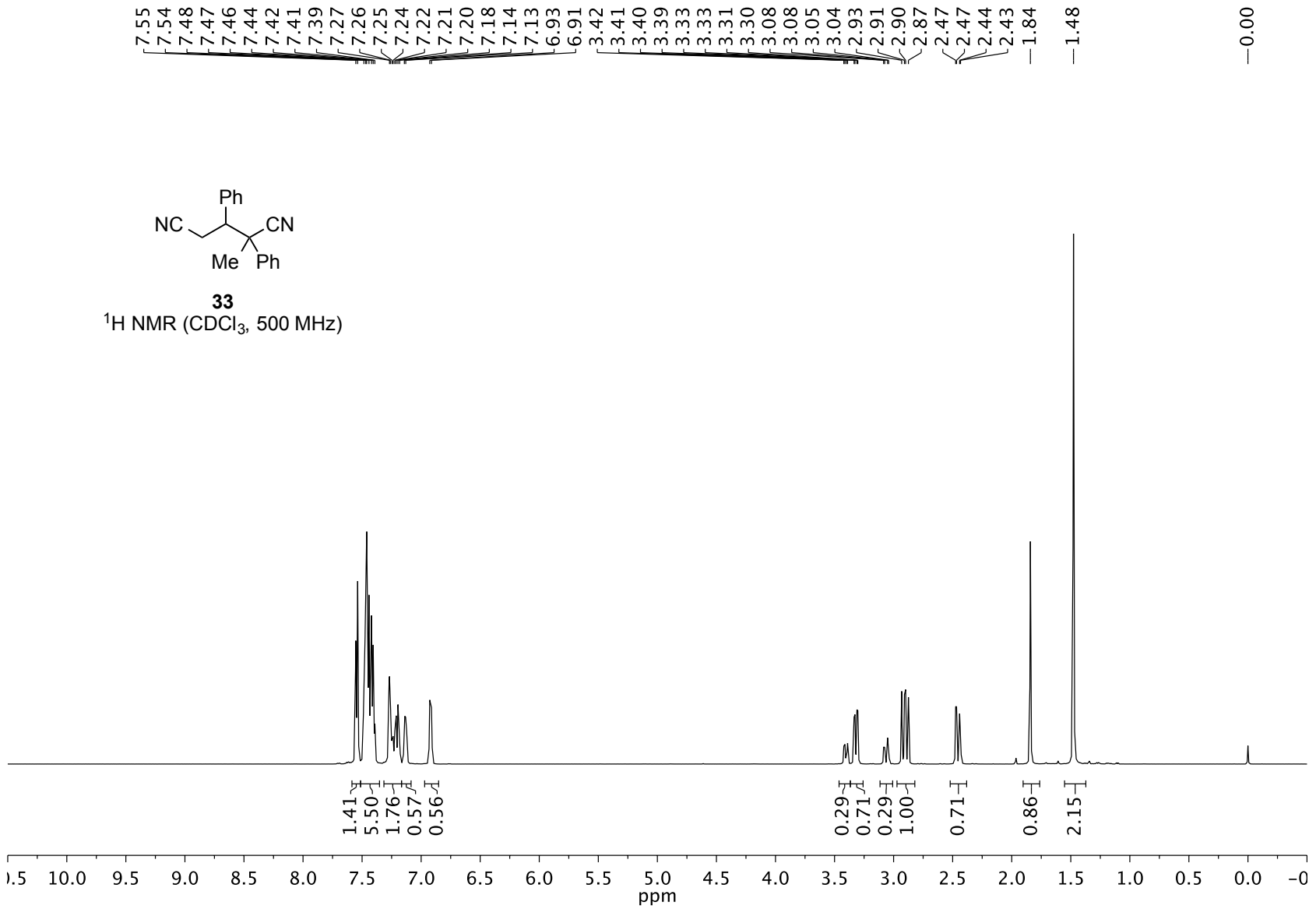


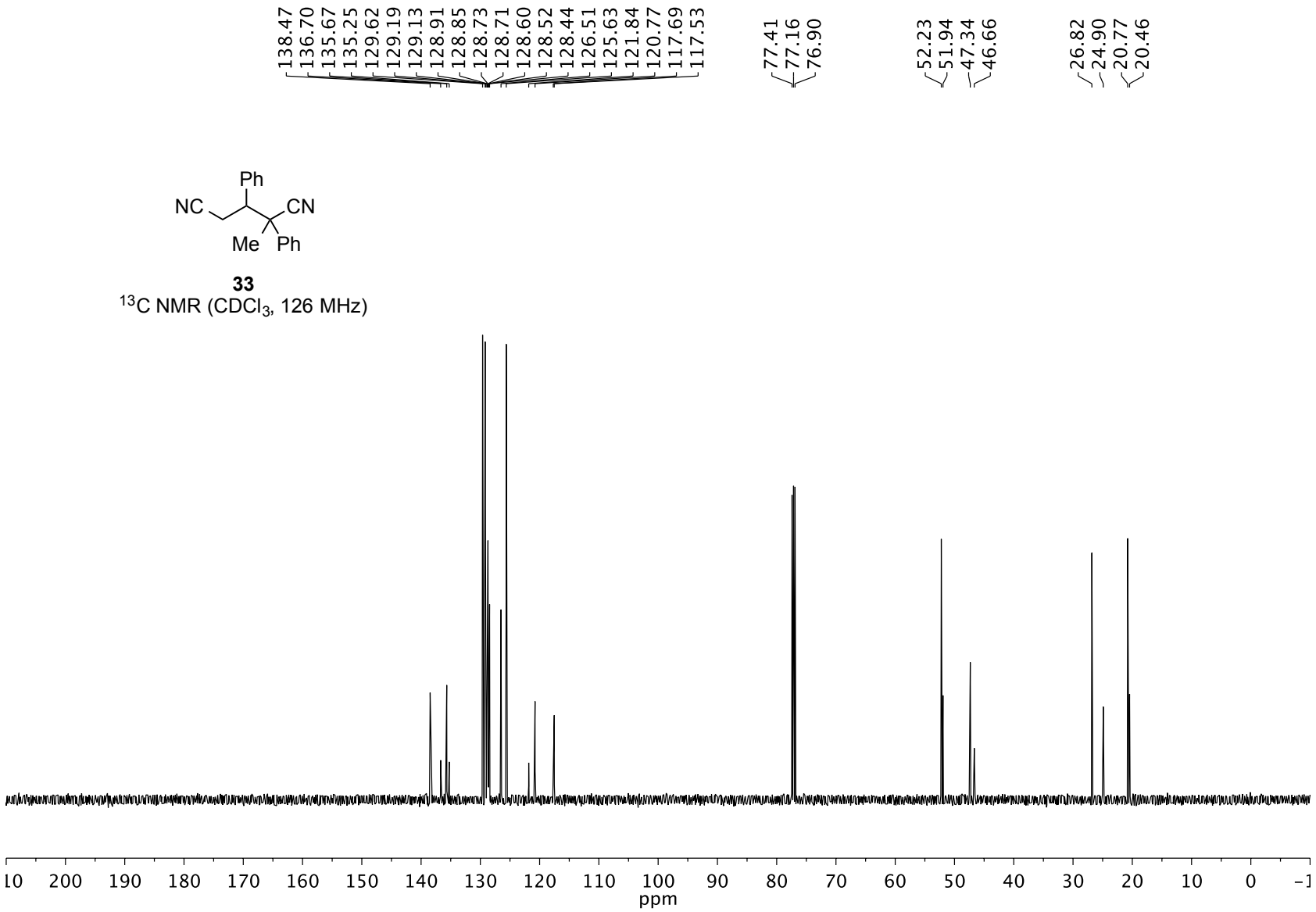
32

^{1}H NMR ($CDCl_3$, 500 MHz)




171.75
170.84
155.85
155.23
150.26
149.61
139.49
138.67
137.44
136.57
129.03
128.70
128.04
127.93
127.72
127.64
124.29
124.00
123.34
122.47
118.20
117.89
77.41
77.16
76.90
57.81
57.46
52.67
52.34
43.62
43.15
23.05
22.72
Ph
O
NC
OMe
N
32
13C NMR (CDCl3, 126 MHz)
ppm

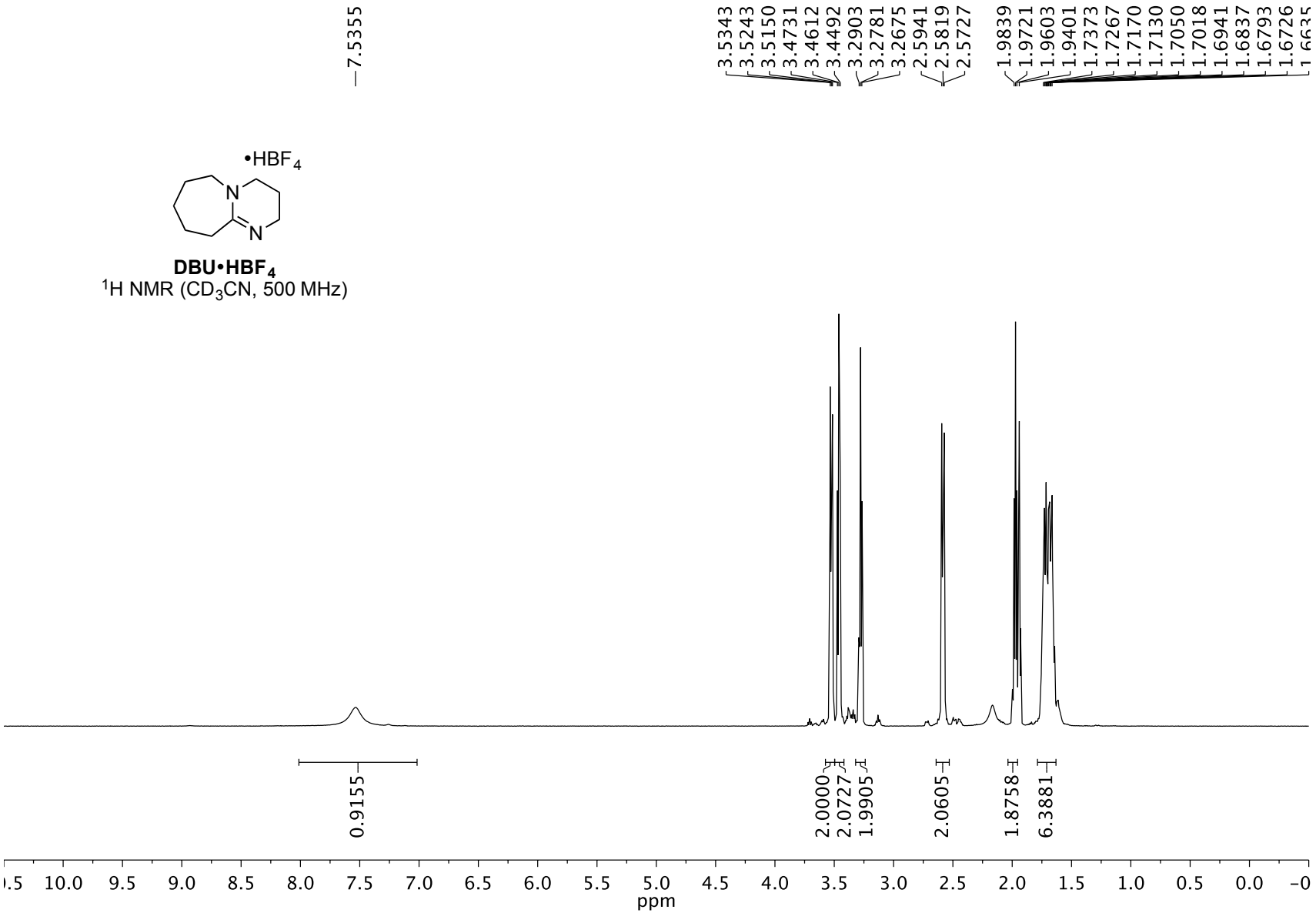

7.55
7.54
7.48
7.47
7.46
7.44
7.42
7.41
7.39
7.27
7.26
7.25
7.24
7.22
7.21
7.20
7.18
7.14
7.13
6.93
6.91
3.42
3.41
3.40
3.39
3.33
3.33
3.31
3.30
3.08
3.08
3.05
3.04
2.93
2.91
2.90
2.87
2.47
2.47
2.44
2.43
1.84
1.48
0.00
Ph
NC
CN
Me
Ph
33
1H NMR (CDCl3, 500 MHz)
1.41
5.50
1.76
0.57
0.56
0.29
0.71
0.29
1.00
0.71
0.86
2.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

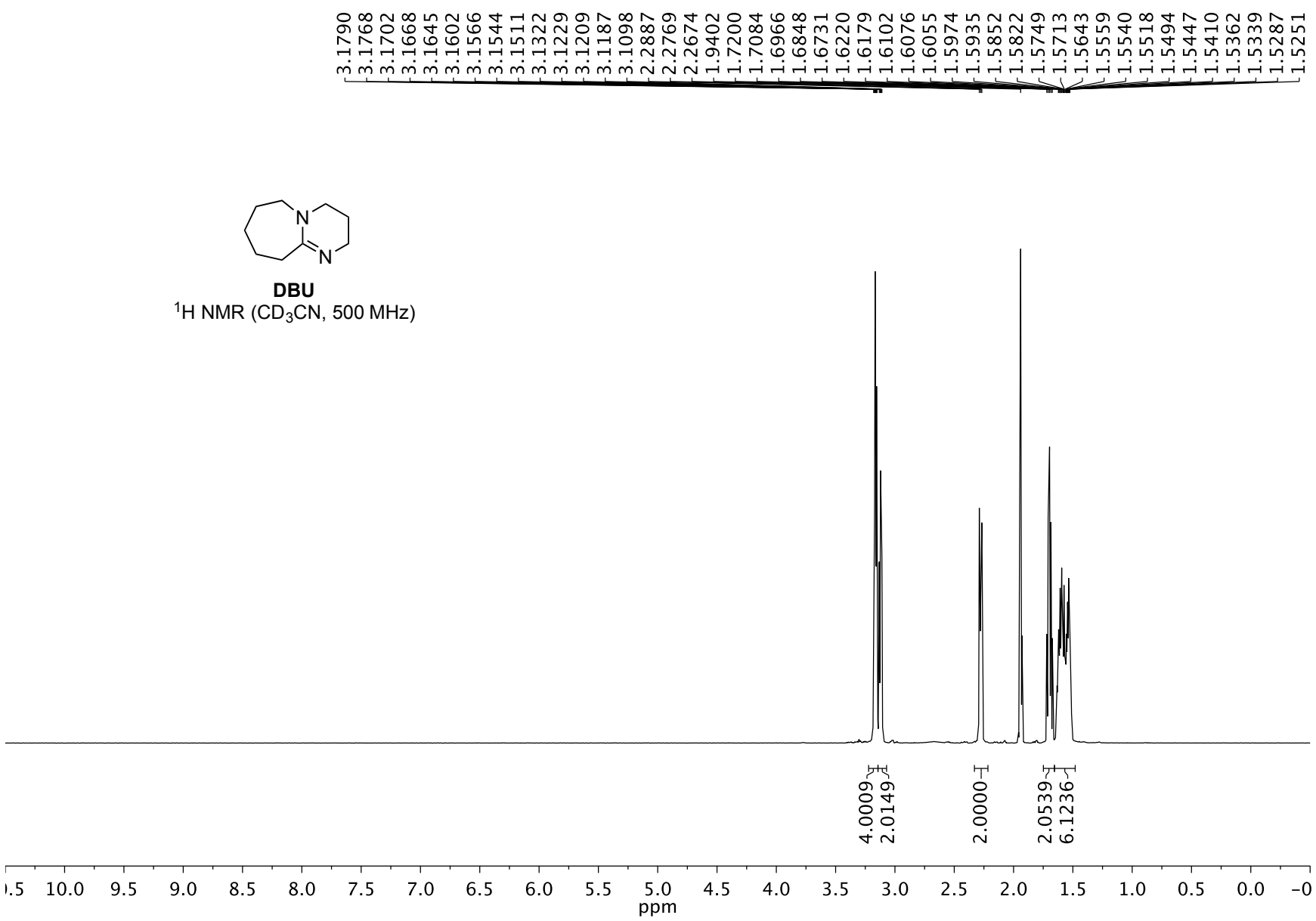


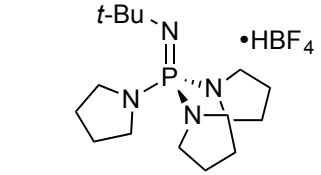
33

^{13}C NMR ($CDCl_3$, 126 MHz)

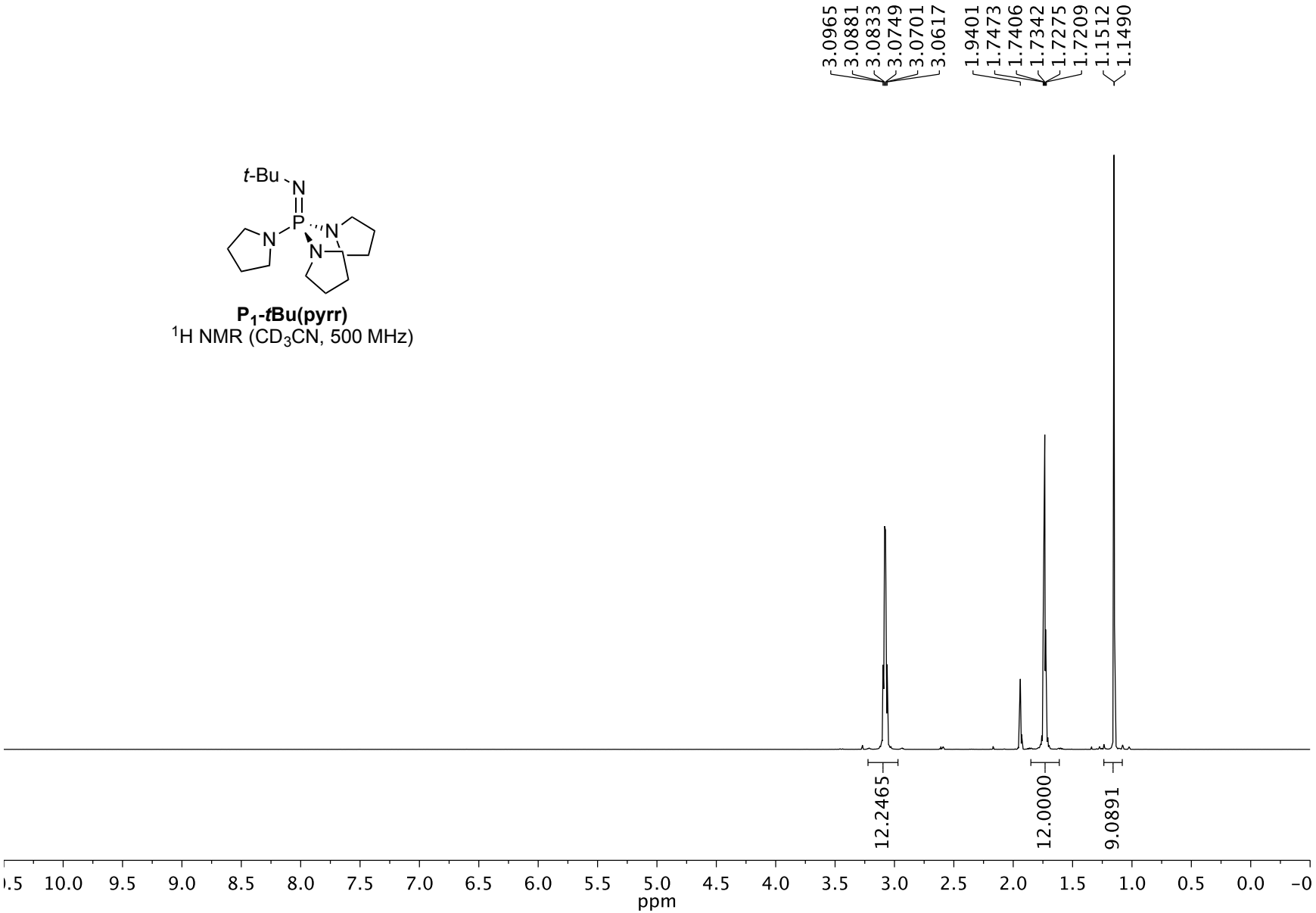
NMR Data for pK_{BH+} Measurements



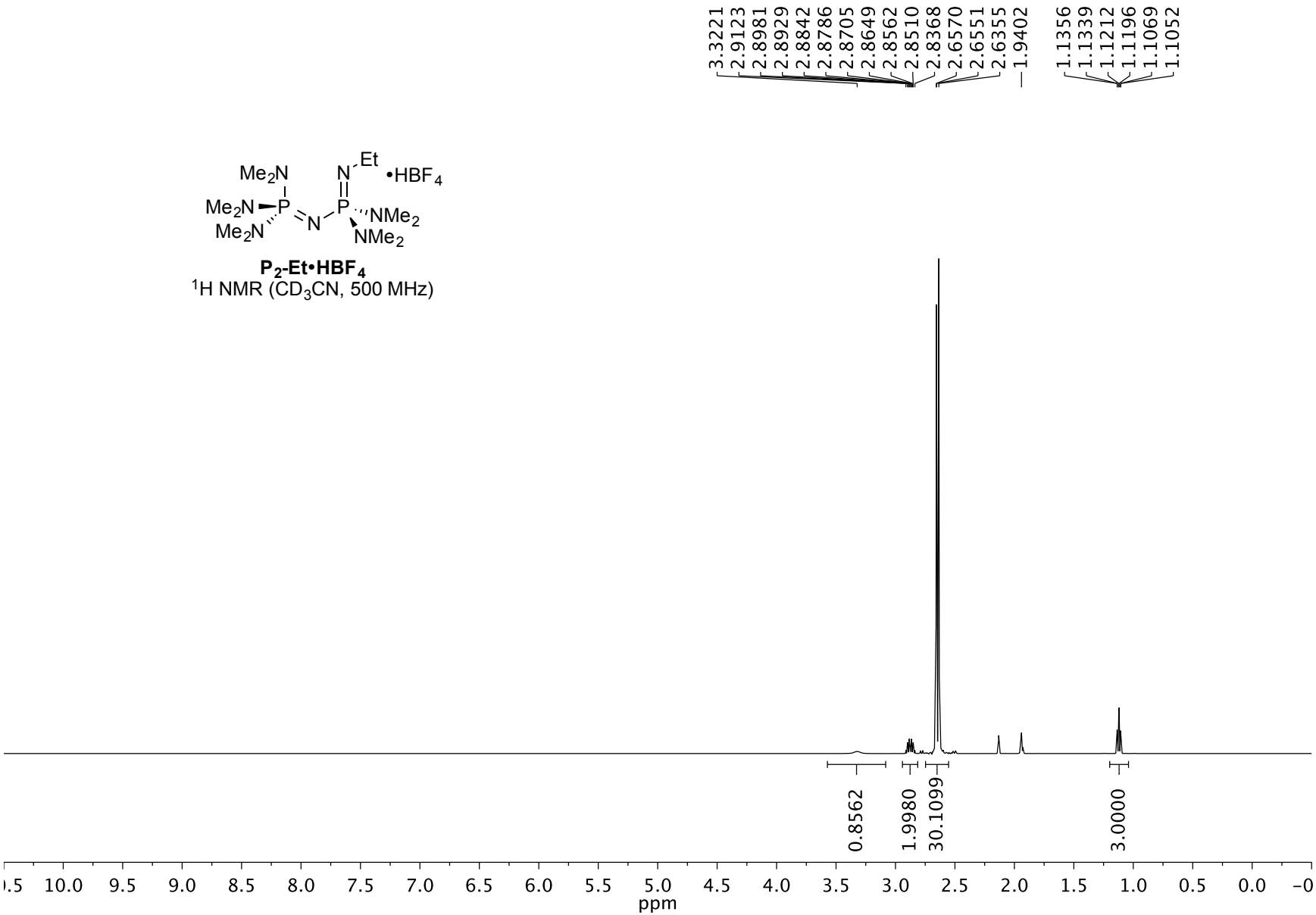

3.1790
3.1768
3.1702
3.1668
3.1645
3.1602
3.1566
3.1544
3.1511
3.1322
3.1229
3.1209
3.1187
3.1098
2.2887
2.2769
2.2674
1.9402
1.7200
1.7084
1.6966
1.6848
1.6731
1.6220
1.6179
1.6102
1.6076
1.6055
1.5974
1.5935
1.5852
1.5822
1.5749
1.5713
1.5643
1.5559
1.5540
1.5518
1.5494
1.5447
1.5410
1.5362
1.5339
1.5287
1.5251
N
N
DBU
1H NMR (CD3CN, 500 MHz)
4.0009
2.0149
2.0000
2.0539
6.1236
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

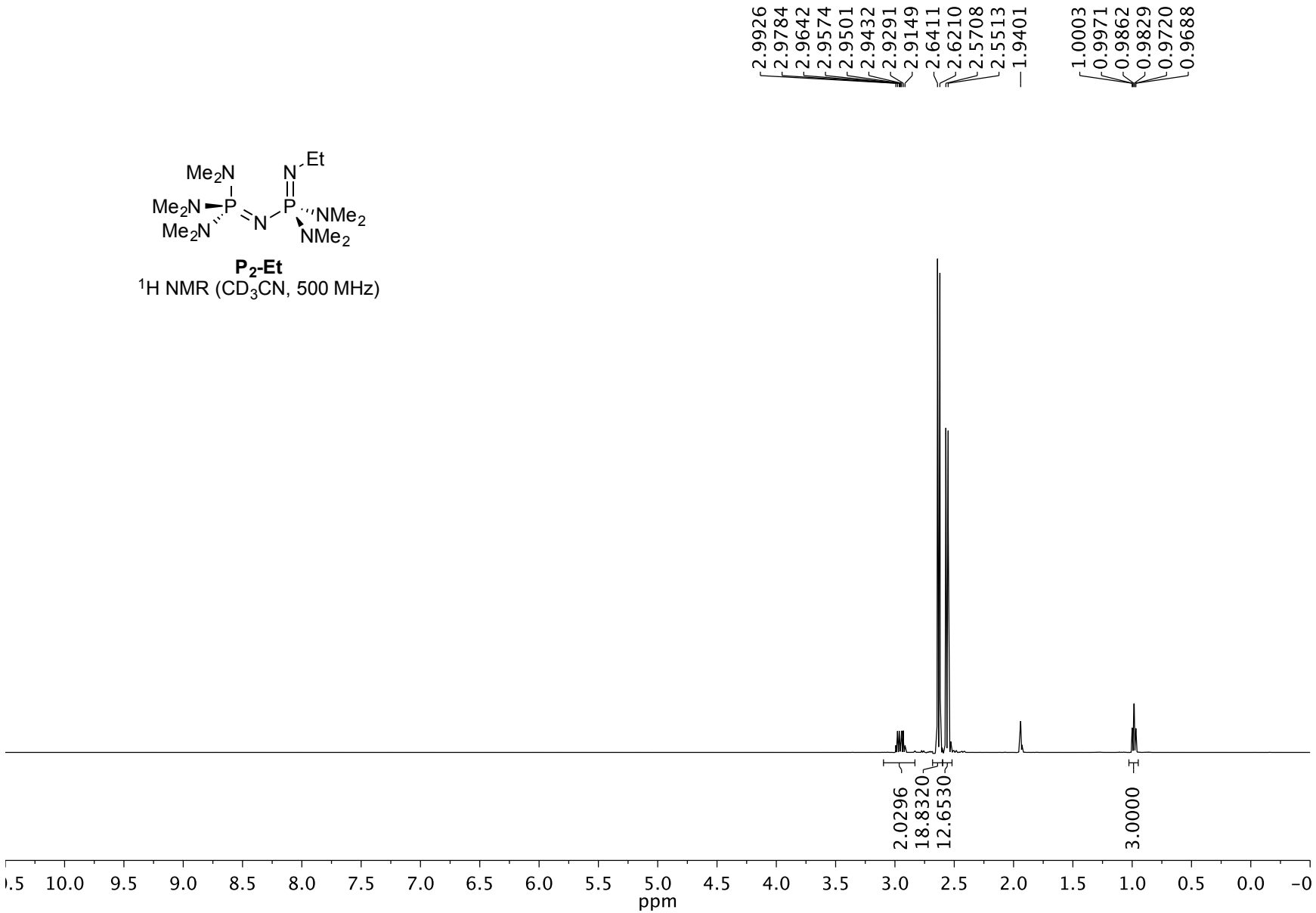


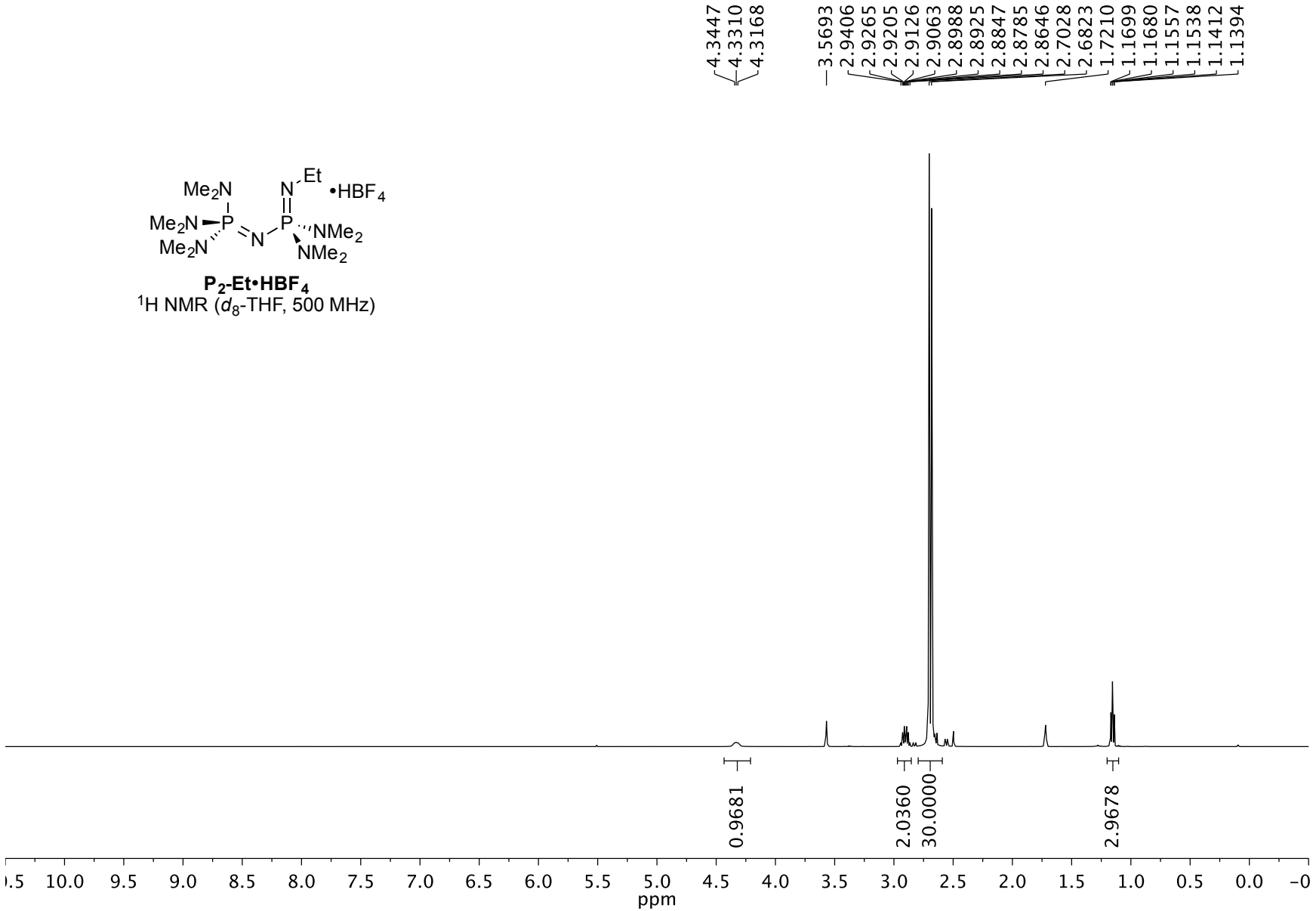
P_1-*t*Bu(pyrr)•HBF_4
^{1}H NMR (CD_3CN, 500 MHz)

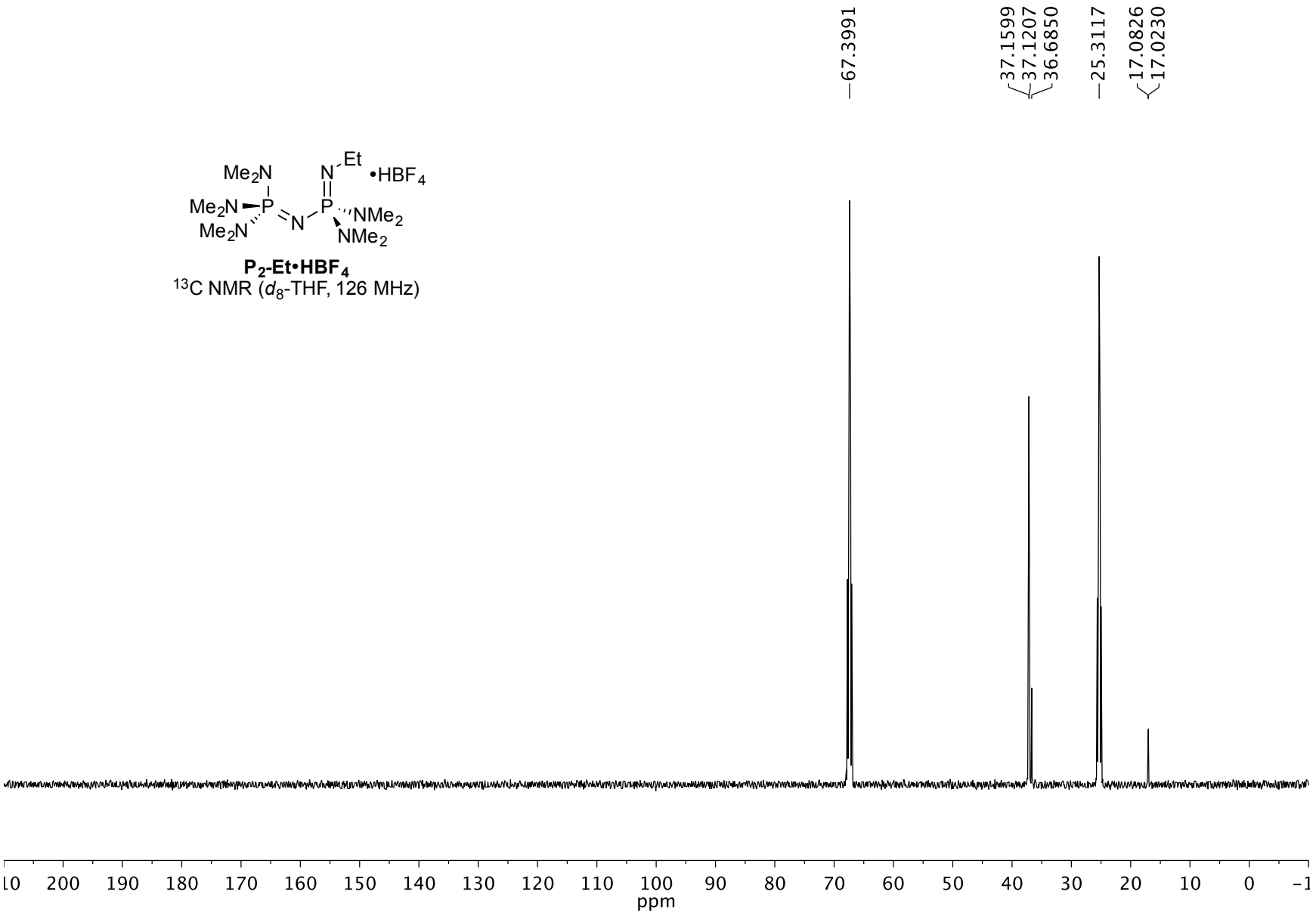


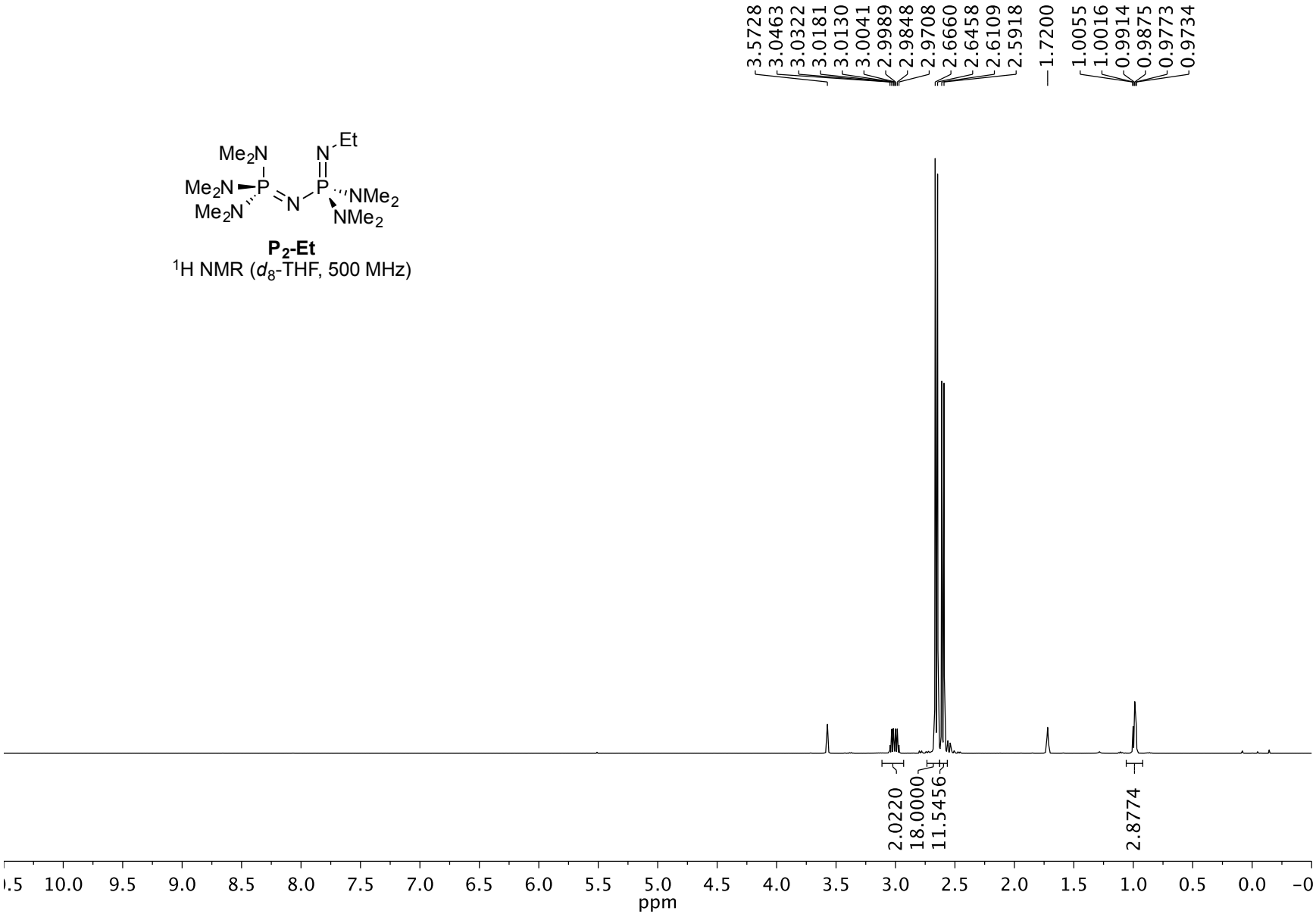
P_1-*t*Bu(pyrr)
^{1}H NMR (CD_3CN, 500 MHz)

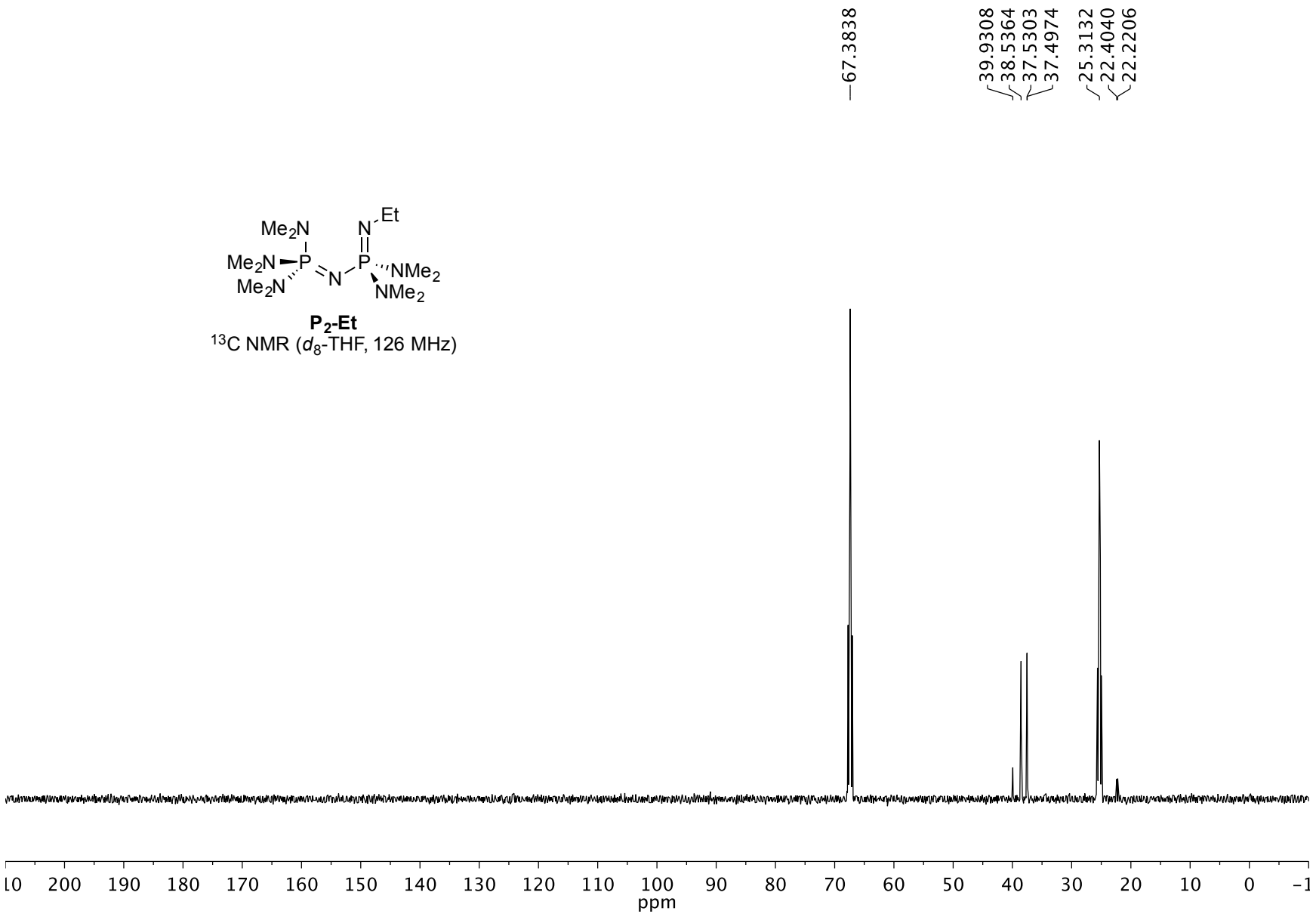

3.3221
2.9123
2.8981
2.8929
2.8842
2.8786
2.8705
2.8649
2.8562
2.8510
2.8368
2.6570
2.6551
2.6355
1.9402
1.1356
1.1339
1.1212
1.1196
1.1069
1.1052
Me2N
N
Et
•HBF4
Me2N
P
N
P
NMe2
Me2N
NMe2
P2-Et•HBF4
1H NMR (CD3CN, 500 MHz)
0.8562
1.9980
30.1099
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

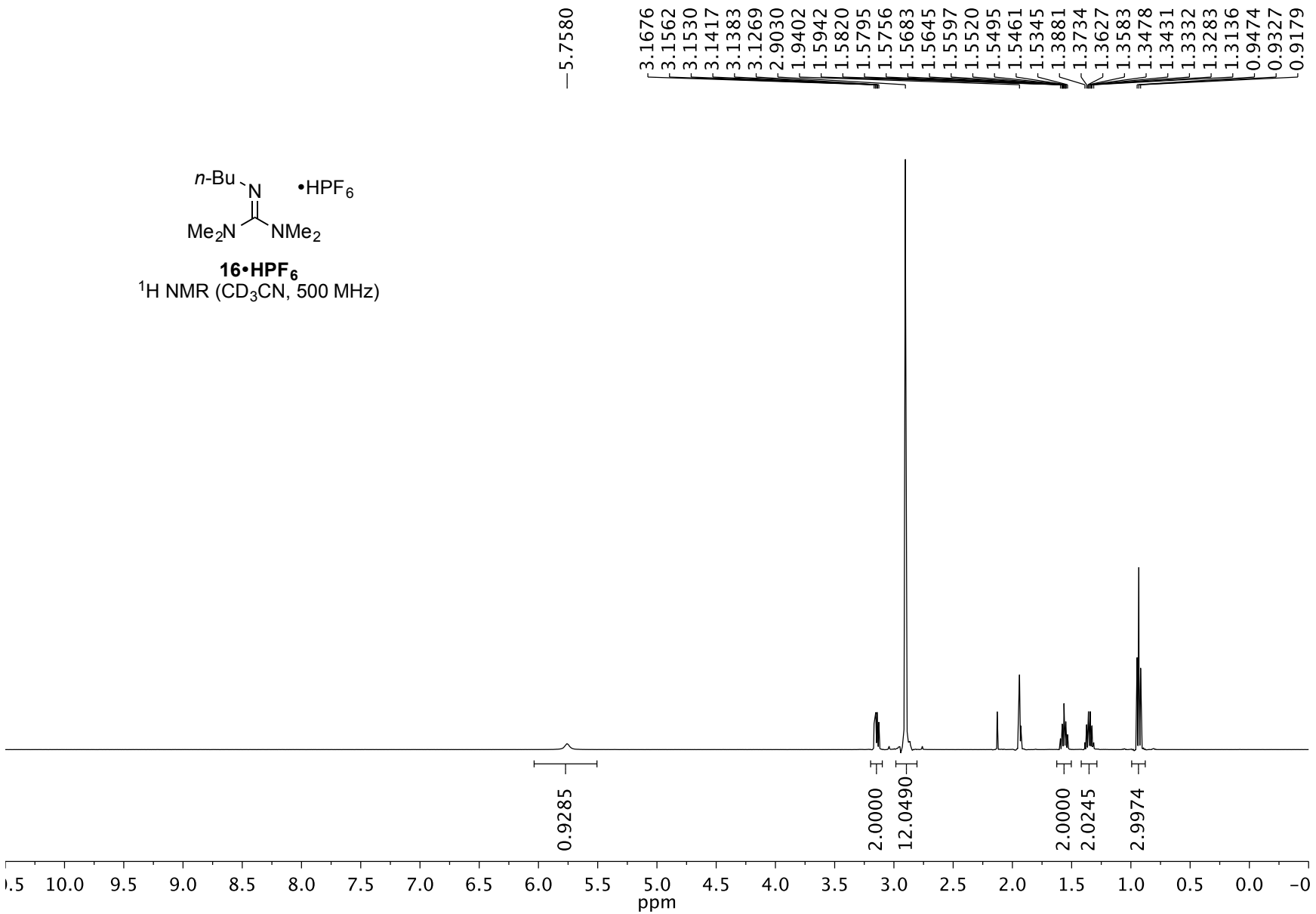

2.9926
2.9784
2.9642
2.9574
2.9501
2.9432
2.9291
2.9149
2.6411
2.6210
2.5708
2.5513
1.9401
1.0003
0.9971
0.9862
0.9829
0.9720
0.9688
Me2N
N
Et
Me2N
P
N
P
NMe2
Me2N
NMe2
P2-Et
1H NMR (CD3CN, 500 MHz)
2.0296
18.8320
12.6530
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

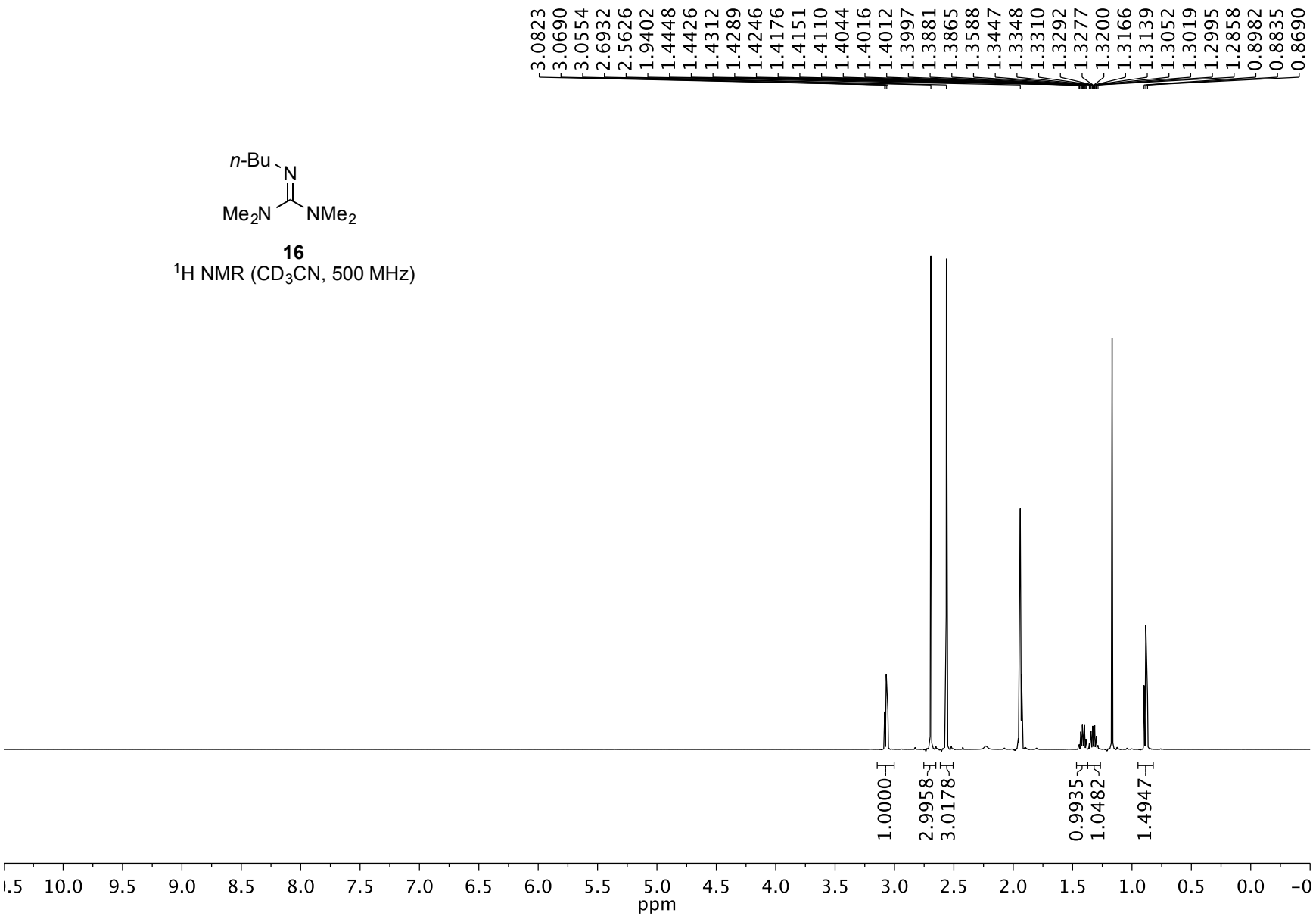

4.3447
4.3310
4.3168
3.5693
2.9406
2.9265
2.9205
2.9126
2.9063
2.8988
2.8925
2.8847
2.8785
2.8646
2.7028
2.6823
1.7210
1.1699
1.1680
1.1557
1.1538
1.1412
1.1394
Me2N
N
Et
•HBF4
Me2N
P
N
P
NMe2
Me2N
NMe2
P2-Et•HBF4
1H NMR (d8-THF, 500 MHz)
0.9681
2.0360
30.0000
2.9678
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

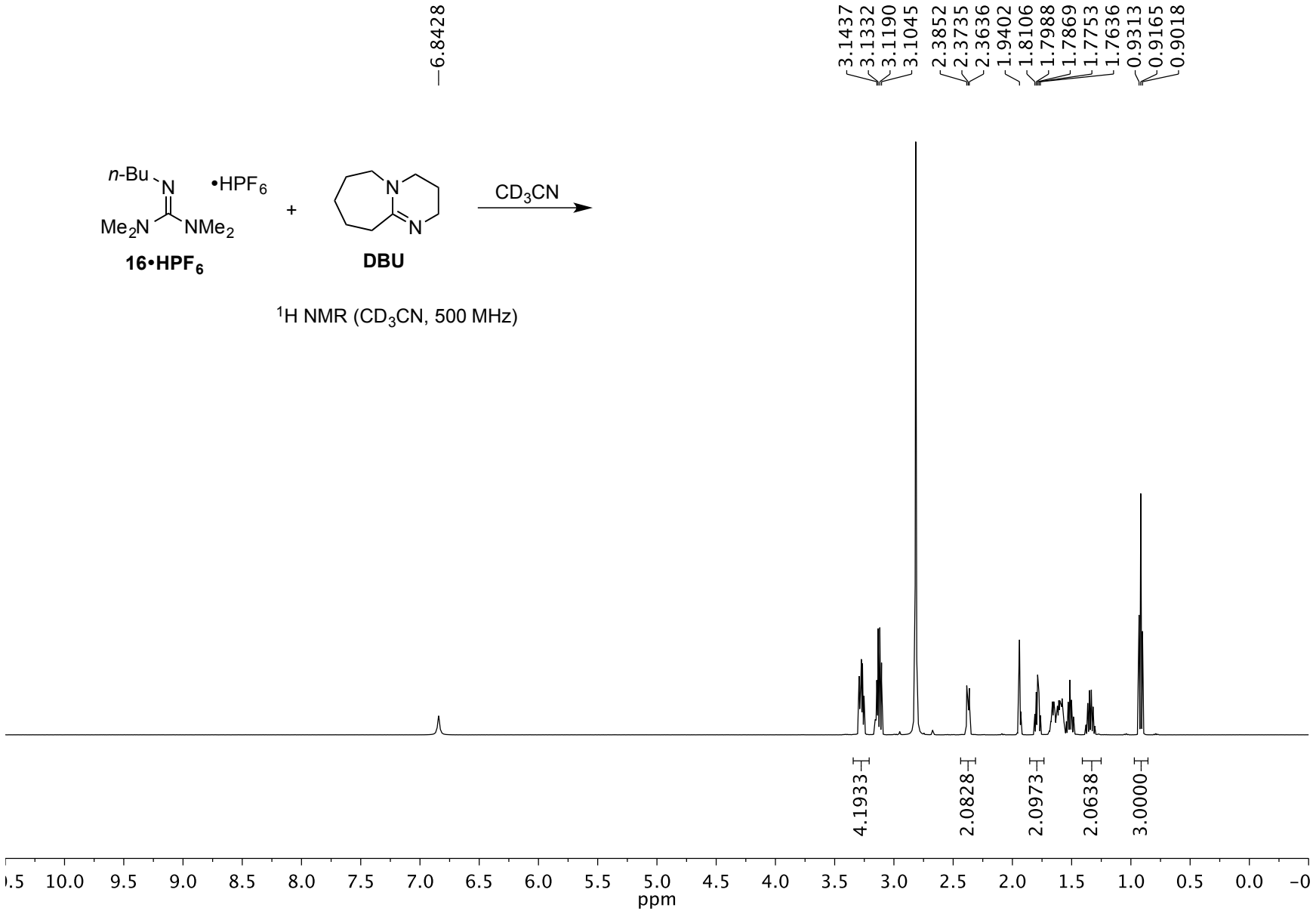

67.3991
37.1599
37.1207
36.6850
25.3117
17.0826
17.0230
Me2N
N
Et
•HBF4
Me2N
P
N
P
NMe2
Me2N
NMe2
P2-Et•HBF4
13C NMR (d8-THF, 126 MHz)
ppm

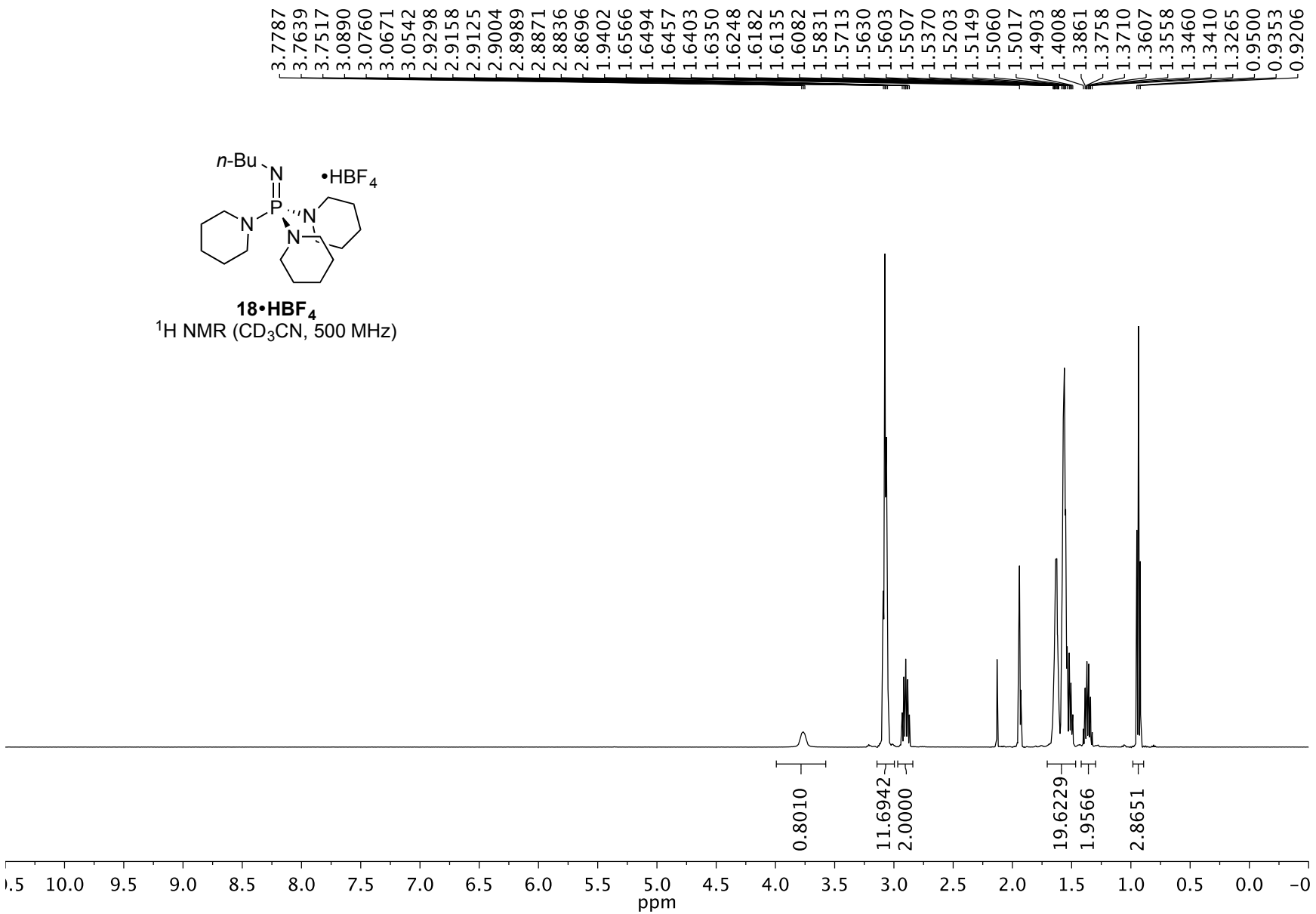

3.5728
3.0463
3.0322
3.0181
3.0130
3.0041
2.9989
2.9848
2.9708
2.6660
2.6458
2.6109
2.5918
1.7200
1.0055
1.0016
0.9914
0.9875
0.9773
0.9734
Me2N
N
Et
Me2N
P
N
P
NMe2
Me2N
NMe2
P2-Et
1H NMR (d8-THF, 500 MHz)
2.0220
18.0000
11.5456
2.8774
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

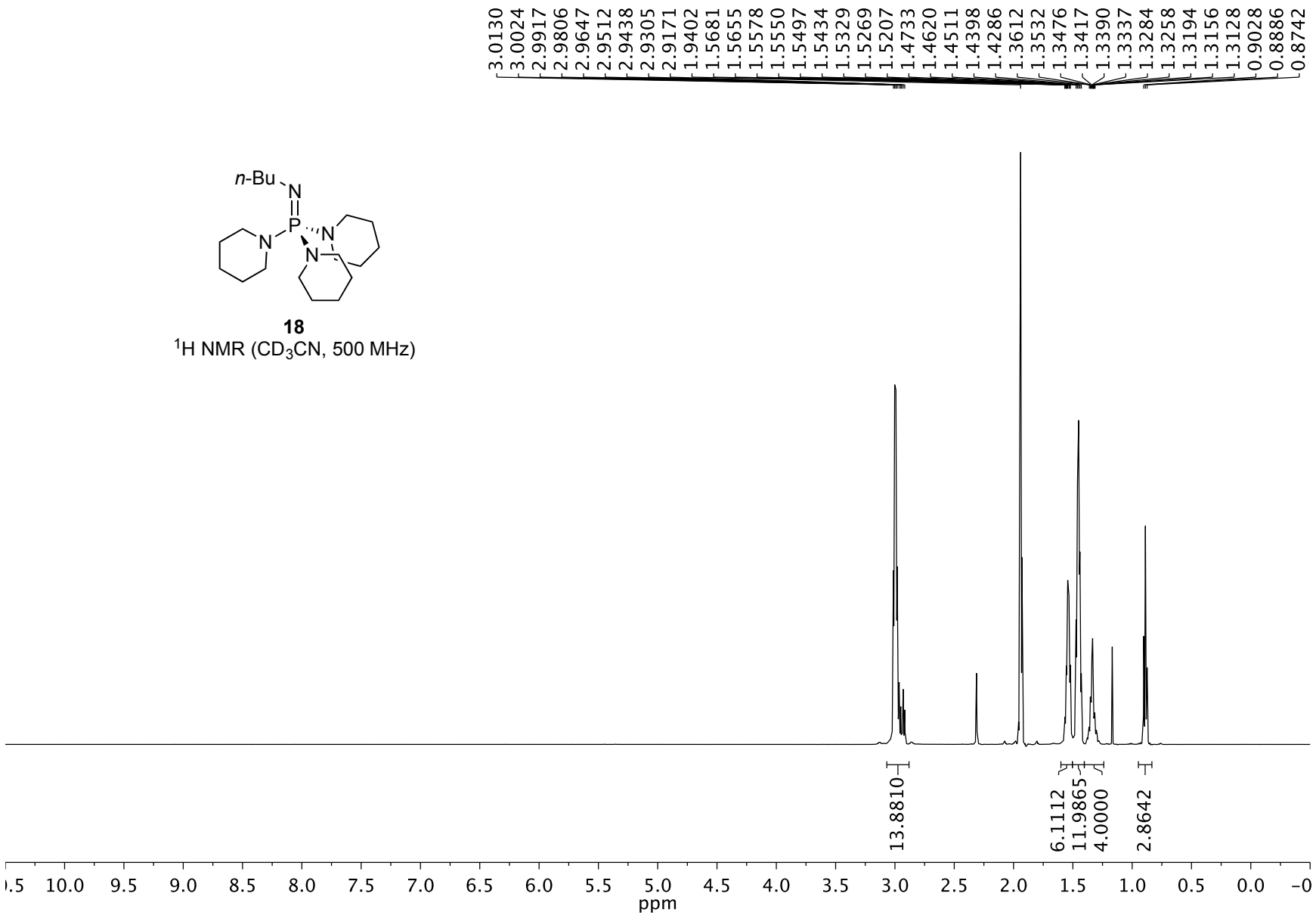

67.3838
39.9308
38.5364
37.5303
37.4974
25.3132
22.4040
22.2206
Me2N
N
Et
Me2N
P
N
P
NMe2
Me2N
NMe2
P2-Et
13C NMR (d8-THF, 126 MHz)
ppm
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

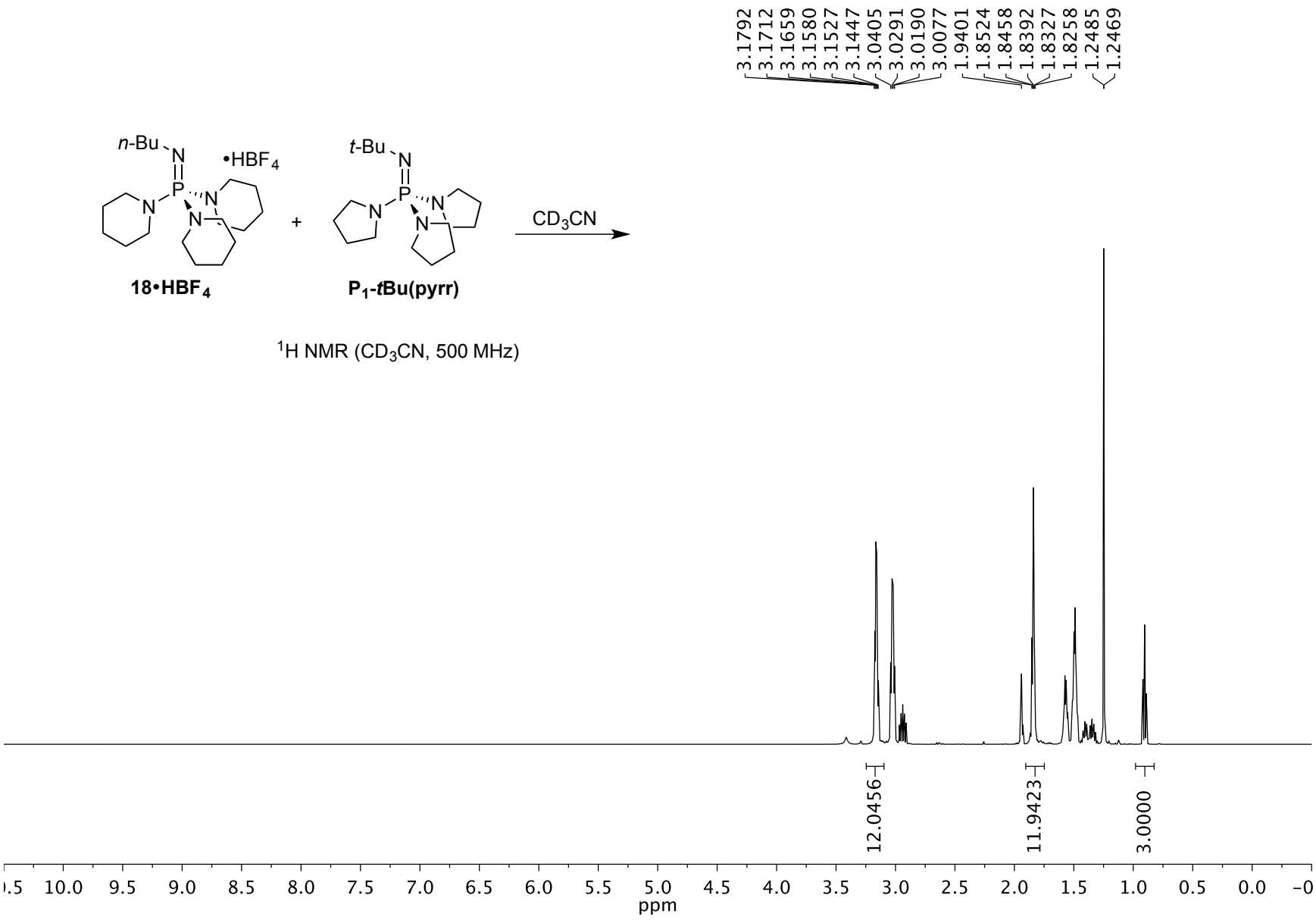

5.7580
3.1676
3.1562
3.1530
3.1417
3.1383
3.1269
2.9030
1.9402
1.5942
1.5820
1.5795
1.5756
1.5683
1.5645
1.5597
1.5520
1.5495
1.5461
1.5345
1.3881
1.3734
1.3627
1.3583
1.3478
1.3431
1.3332
1.3283
1.3136
0.9474
0.9327
0.9179
n-Bu
N
•HPF6
Me2N
NMe2
16•HPF6
1H NMR (CD3CN, 500 MHz)
0.9285
2.0000
12.0490
2.0000
2.0245
2.9974
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

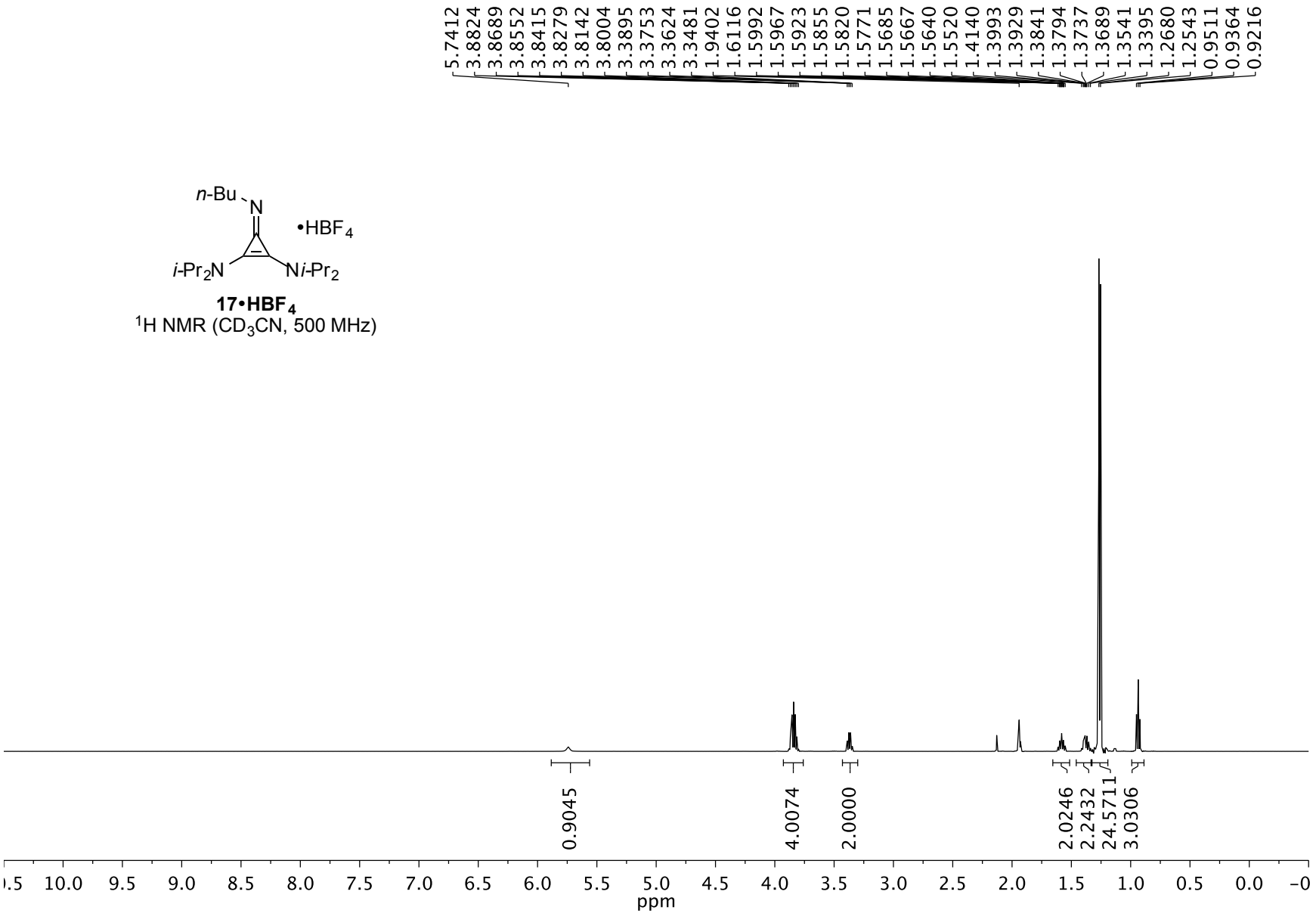

3.0823
3.0690
3.0554
2.6932
2.5626
1.9402
1.4448
1.4426
1.4312
1.4289
1.4246
1.4176
1.4151
1.4110
1.4044
1.4016
1.4012
1.3997
1.3881
1.3865
1.3588
1.3447
1.3348
1.3310
1.3292
1.3277
1.3200
1.3166
1.3139
1.3052
1.3019
1.2995
1.2858
0.8982
0.8835
0.8690
n-Bu
N
Me2N
NMe2
16
1H NMR (CD3CN, 500 MHz)
1.0000
2.9958
3.0178
0.9935
1.0482
1.4947
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

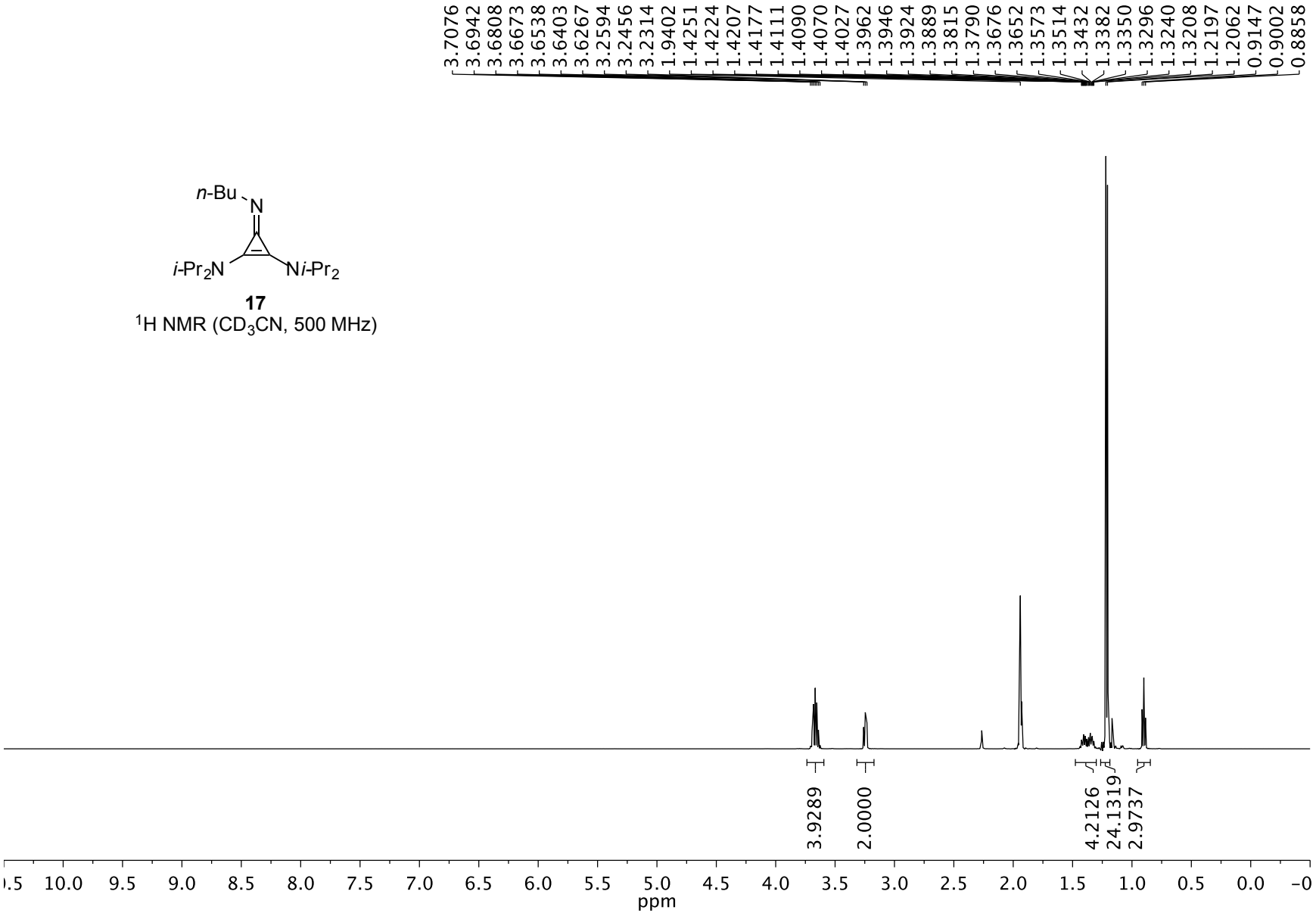

6.8428
3.1437
3.1332
3.1190
3.1045
2.3852
2.3735
2.3636
1.9402
1.8106
1.7988
1.7869
1.7753
1.7636
0.9313
0.9165
0.9018
n-Bu
N
•HPF6
Me2N
NMe2
16•HPF6
+
N
N
DBU
CD3CN
1H NMR (CD3CN, 500 MHz)
4.1933
2.0828
2.0973
2.0638
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


3.7787
3.7639
3.7517
3.0890
3.0760
3.0671
3.0542
2.9298
2.9158
2.9125
2.9004
2.8989
2.8871
2.8836
2.8696
1.9402
1.6566
1.6494
1.6457
1.6403
1.6350
1.6248
1.6182
1.6135
1.6082
1.5831
1.5713
1.5630
1.5603
1.5507
1.5370
1.5203
1.5149
1.5060
1.5017
1.4903
1.4008
1.3861
1.3758
1.3710
1.3607
1.3558
1.3460
1.3410
1.3265
0.9500
0.9353
0.9206
n-Bu
N
•HBF4
P
N
N
N
18•HBF4
1H NMR (CD3CN, 500 MHz)
0.8010
11.6942
2.0000
19.6229
1.9566
2.8651
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


3.0130
3.0024
2.9917
2.9806
2.9647
2.9512
2.9438
2.9305
2.9171
1.9402
1.5681
1.5655
1.5578
1.5550
1.5497
1.5434
1.5329
1.5269
1.5207
1.4733
1.4620
1.4511
1.4398
1.4286
1.3612
1.3532
1.3476
1.3417
1.3390
1.3337
1.3284
1.3258
1.3194
1.3156
1.3128
0.9028
0.8886
0.8742
n-Bu
N
P
N
N
N
18
1H NMR (CD3CN, 500 MHz)
13.8810
6.1112
11.9865
4.0000
2.8642
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

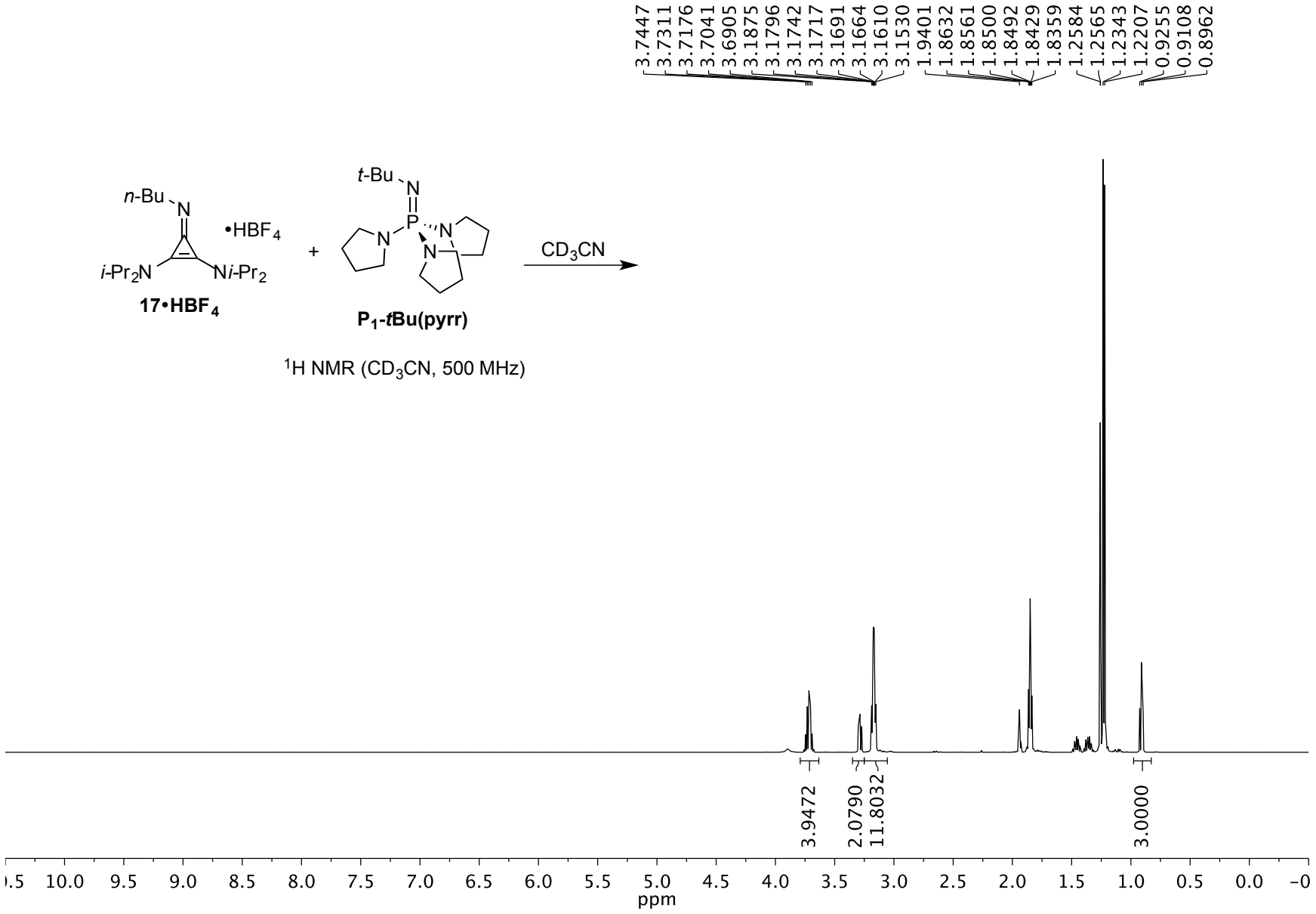

3.1792
3.1712
3.1659
3.1580
3.1527
3.1447
3.0405
3.0291
3.0190
3.0077
1.9401
1.8524
1.8458
1.8392
1.8327
1.8258
1.2485
1.2469
n-Bu
•HBF4
t-Bu
CD3CN
18•HBF4
P1-tBu(pyrr)
1H NMR (CD3CN, 500 MHz)
12.0456
11.9423
3.0000
ppm

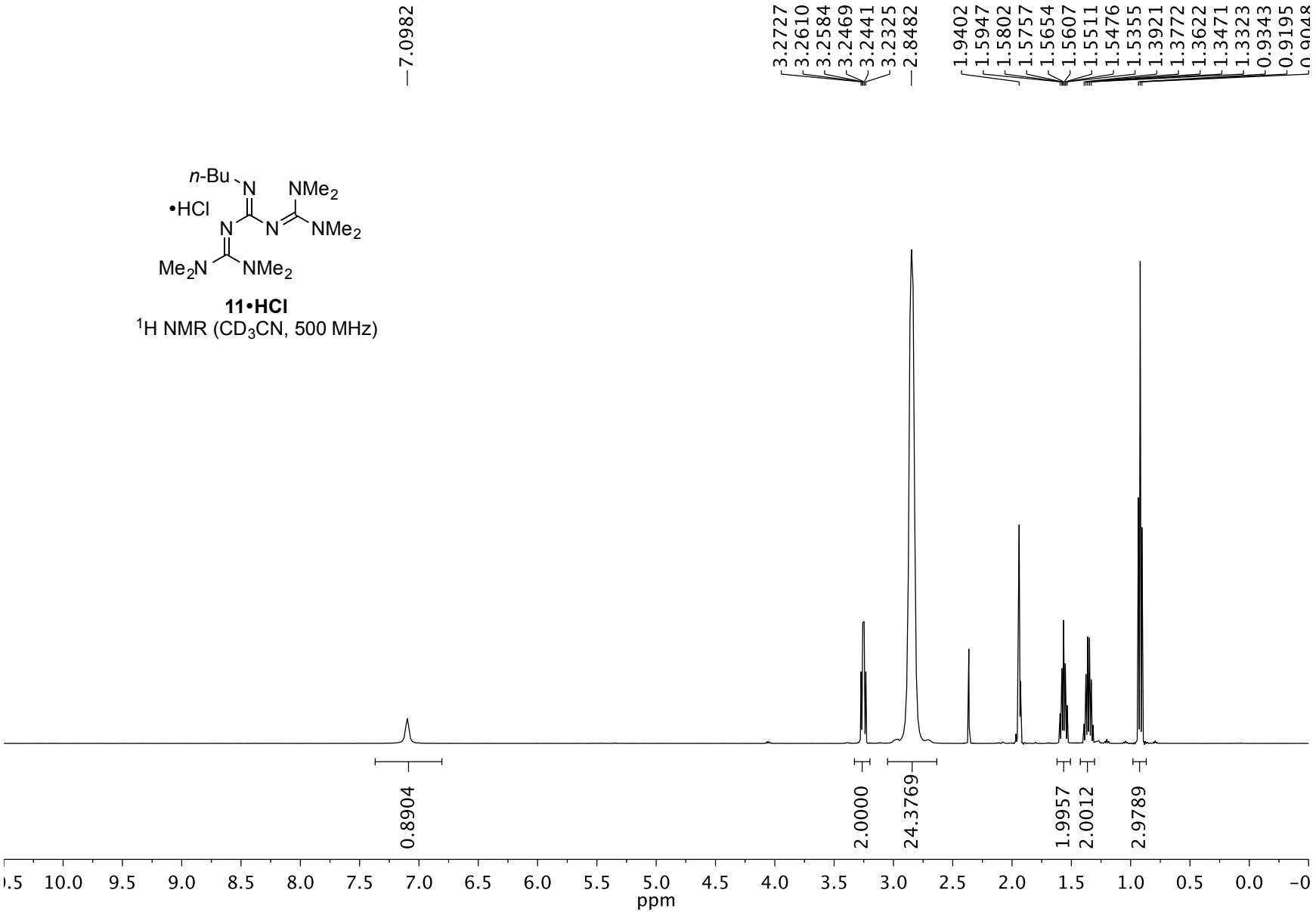

5.7412
3.8824
3.8689
3.8552
3.8415
3.8279
3.8142
3.8004
3.3895
3.3753
3.3624
3.3481
1.9402
1.6116
1.5992
1.5967
1.5923
1.5855
1.5820
1.5771
1.5685
1.5667
1.5640
1.5520
1.4140
1.3993
1.3929
1.3841
1.3794
1.3737
1.3689
1.3541
1.3395
1.2680
1.2543
0.9511
0.9364
0.9216
n-Bu
N
•HBF4
i-Pr2N
Ni-Pr2
17•HBF4
1H NMR (CD3CN, 500 MHz)
0.9045
4.0074
2.0000
2.0246
2.2432
24.5711
3.0306
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm

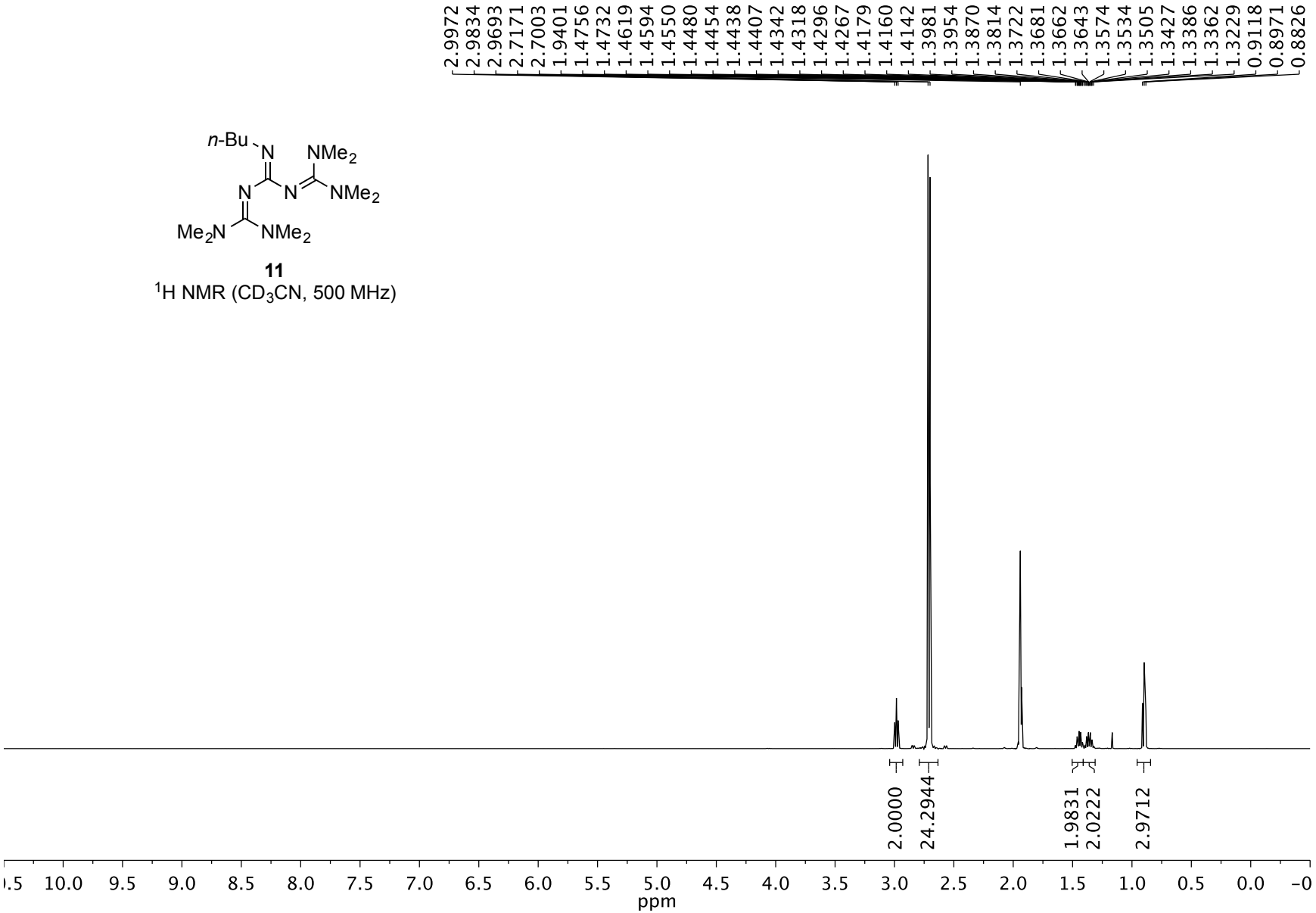


17

^{1}H NMR (CD_3CN, 500 MHz)

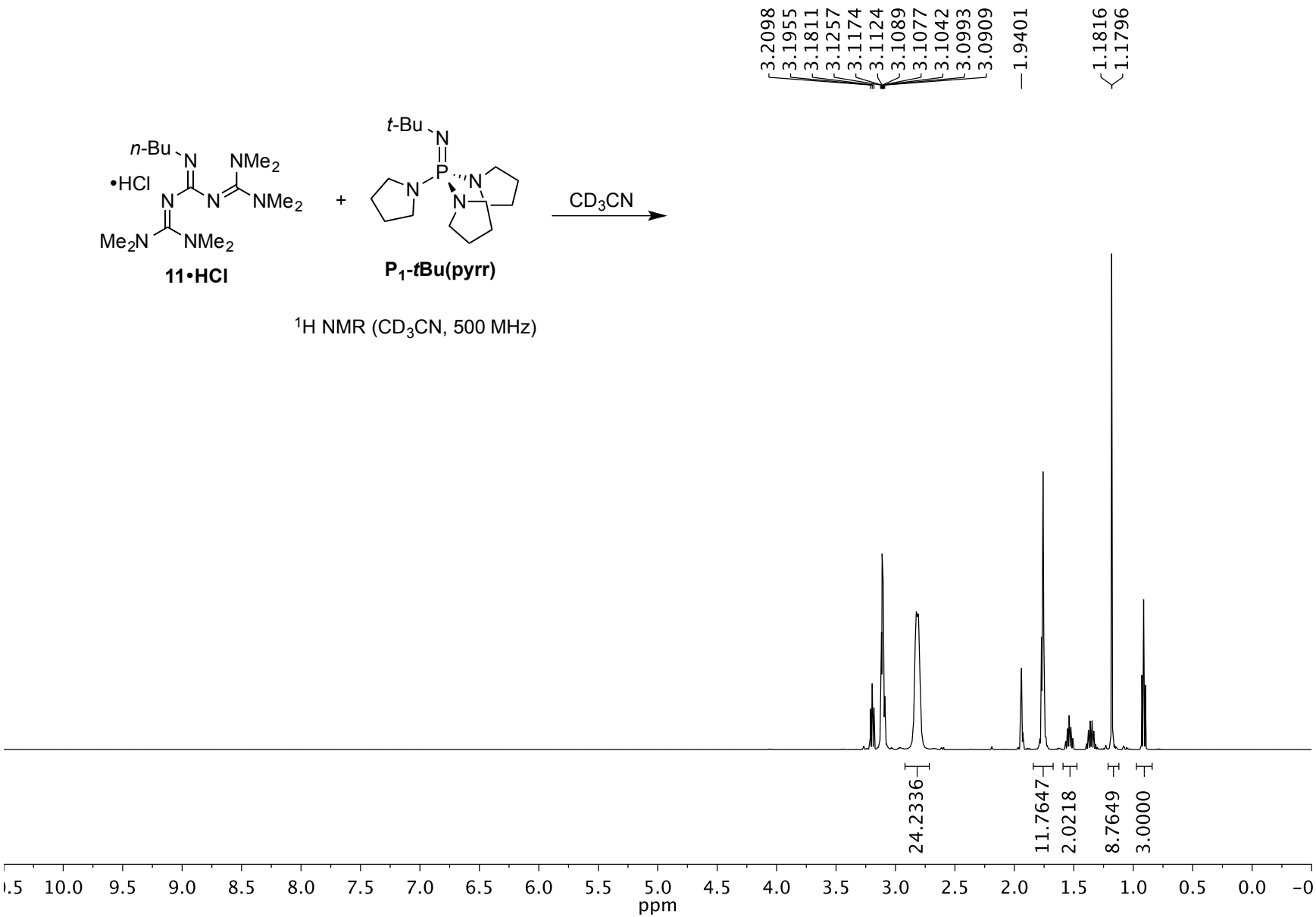

3.7447
3.7311
3.7176
3.7041
3.6905
3.1875
3.1796
3.1742
3.1717
3.1691
3.1664
3.1610
3.1530
1.9401
1.8632
1.8561
1.8500
1.8492
1.8429
1.8359
1.2584
1.2565
1.2343
1.2207
0.9255
0.9108
0.8962
n-Bu
N
•HBF4
i-Pr2N
Ni-Pr2
17•HBF4
+
t-Bu
N
P
N
N
N
P1-tBu(pyrr)
CD3CN
1H NMR (CD3CN, 500 MHz)
3.9472
2.0790
11.8032
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


7.0982
3.2727
3.2610
3.2584
3.2469
3.2441
3.2325
2.8482
1.9402
1.5947
1.5802
1.5757
1.5654
1.5607
1.5511
1.5476
1.5355
1.3921
1.3772
1.3622
1.3471
1.3323
0.9343
0.9195
n-Bu
NMe2
•HCl
N
N
N
NMe2
Me2N
NMe2
11•HCl
1H NMR (CD3CN, 500 MHz)
0.8904
2.0000
24.3769
1.9957
2.0012
2.9789
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

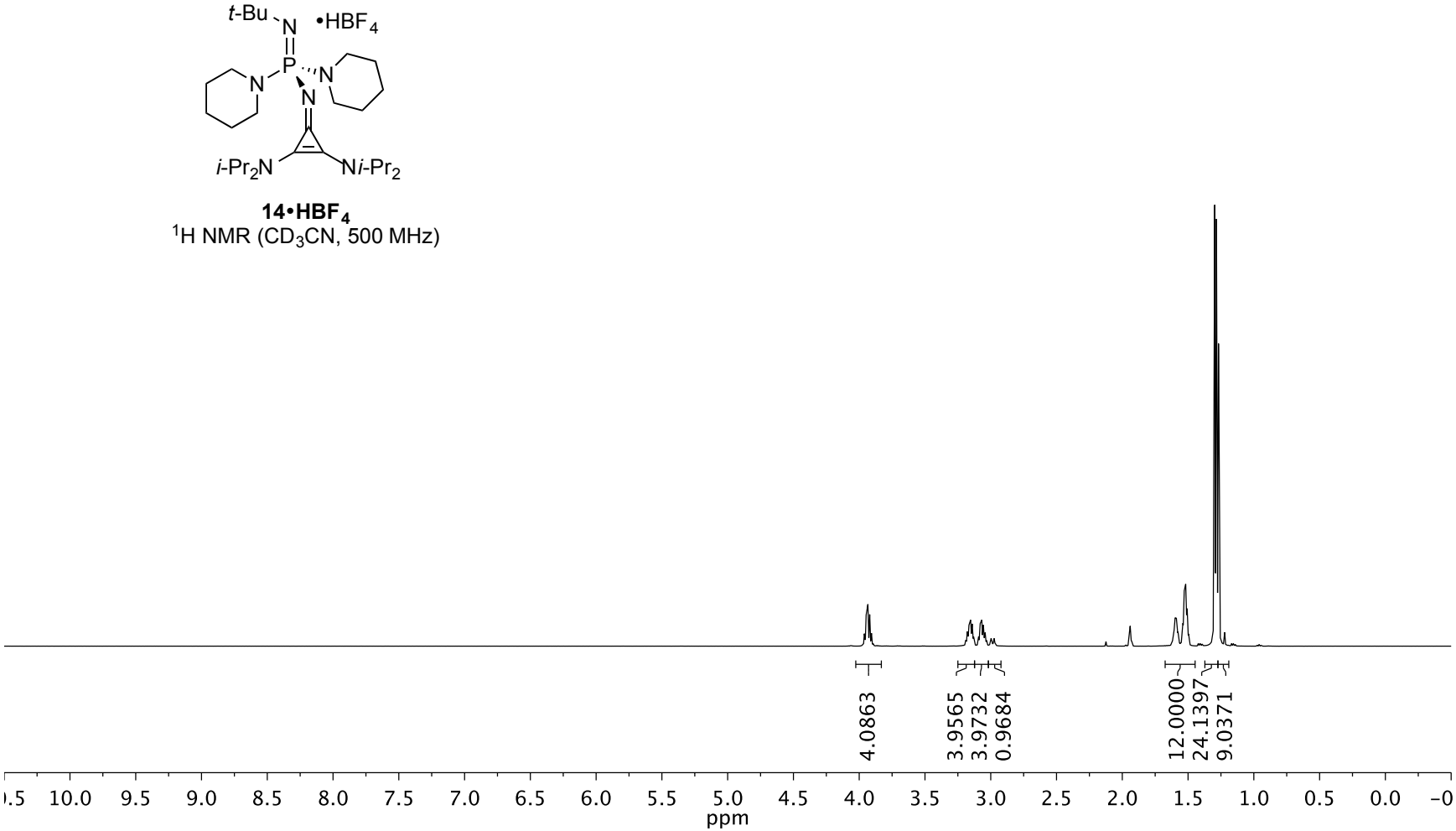


11

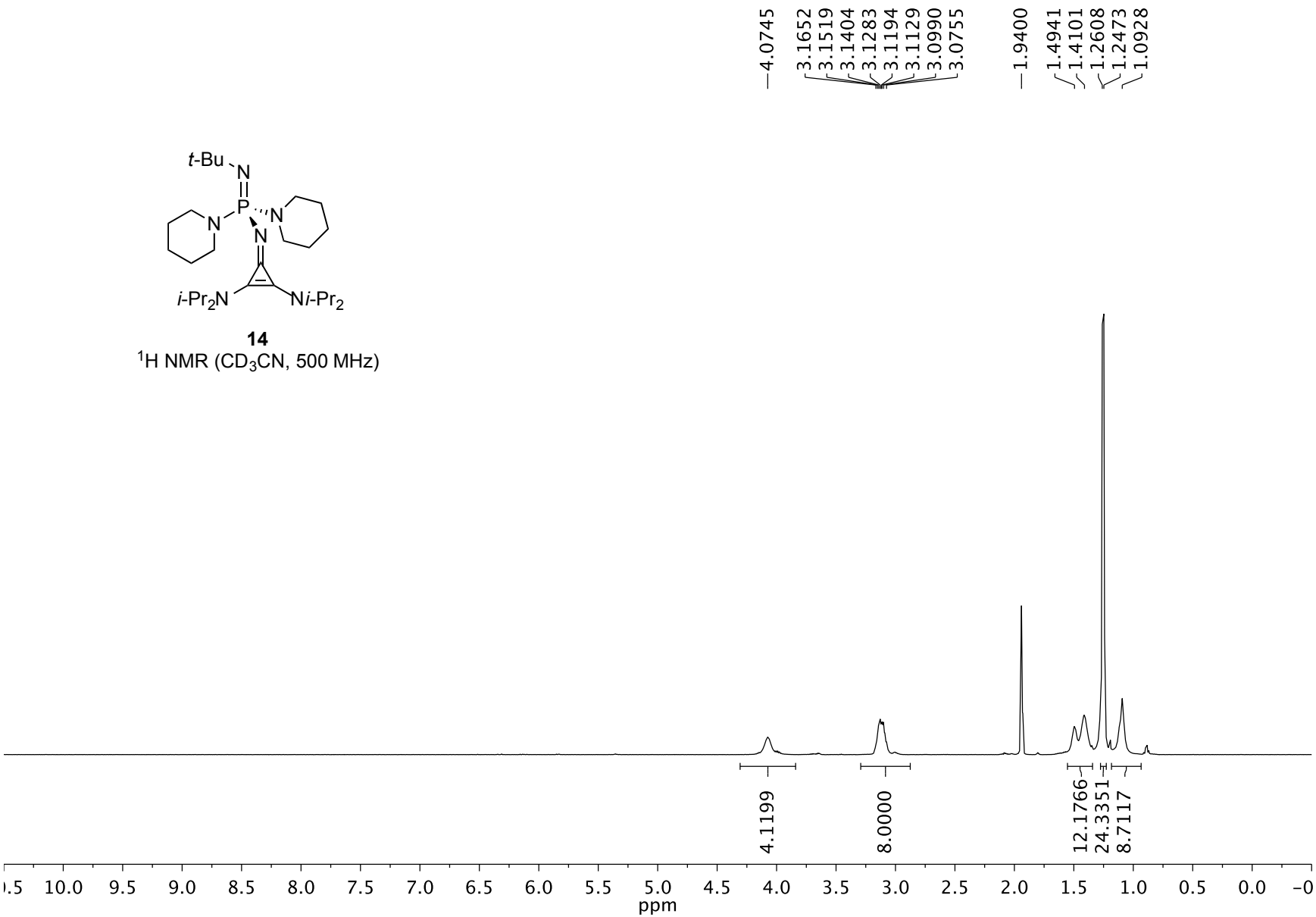
^{1}H NMR (CD_3CN, 500 MHz)



^{1}H NMR (CD_3CN, 500 MHz)

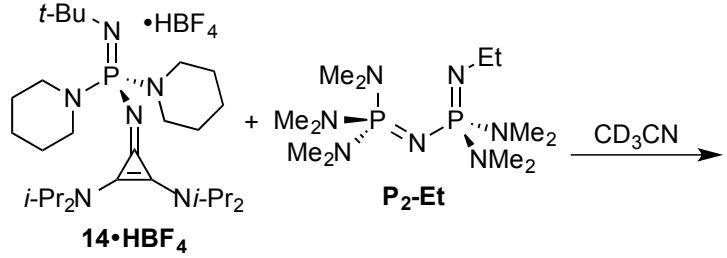


14•HBF$_4$
^{1}H NMR (CD_3CN, 500 MHz)



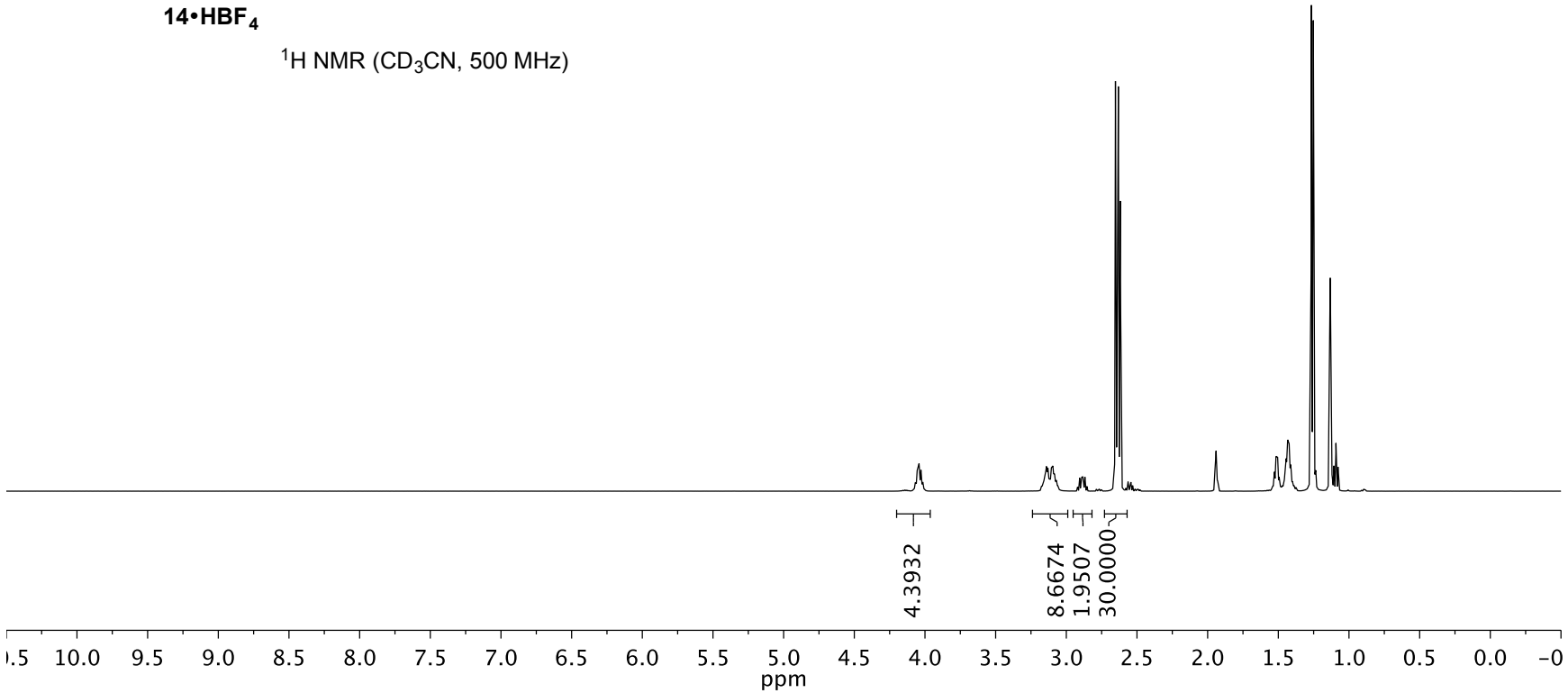
14

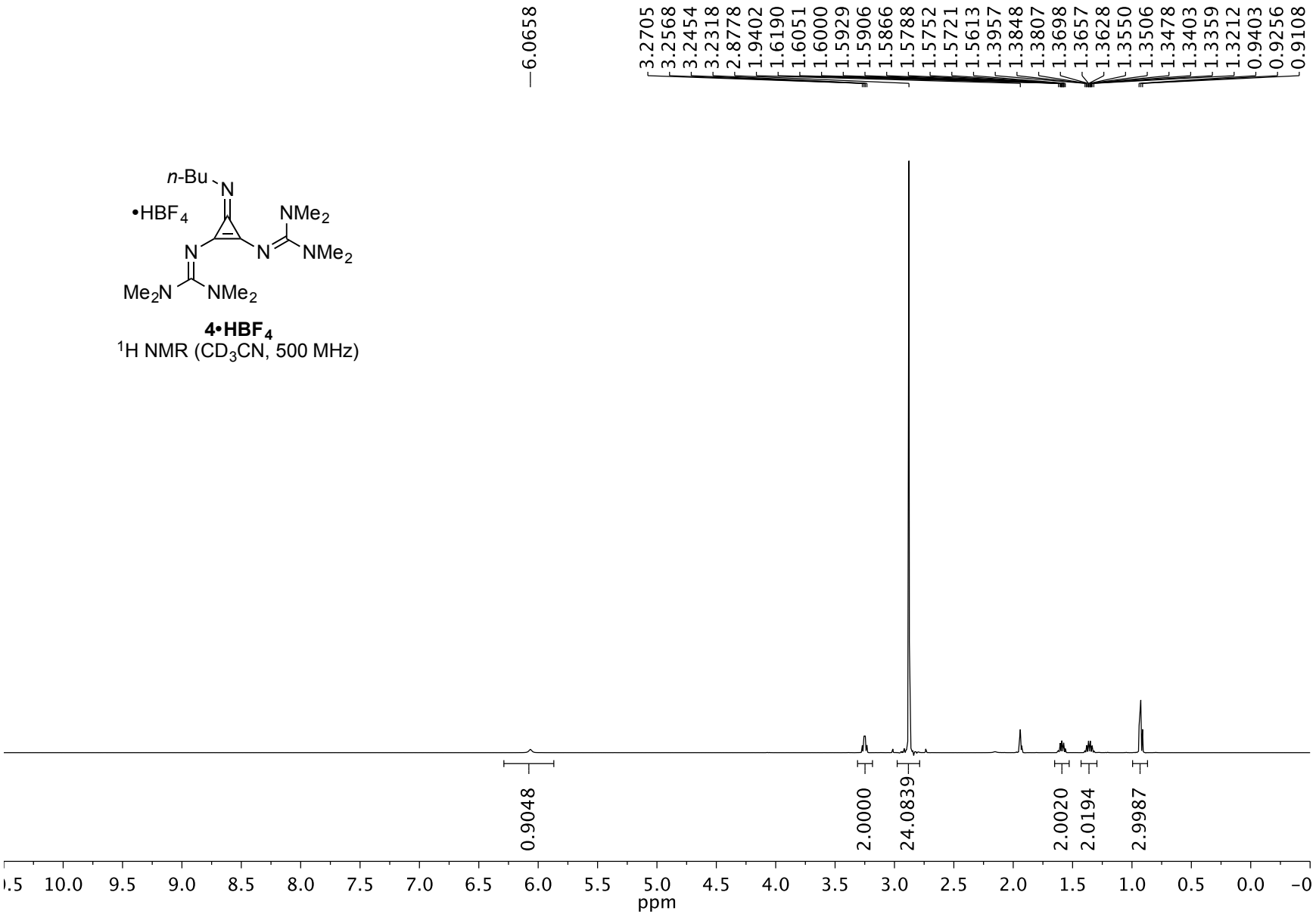
^{1}H NMR (CD_3CN, 500 MHz)

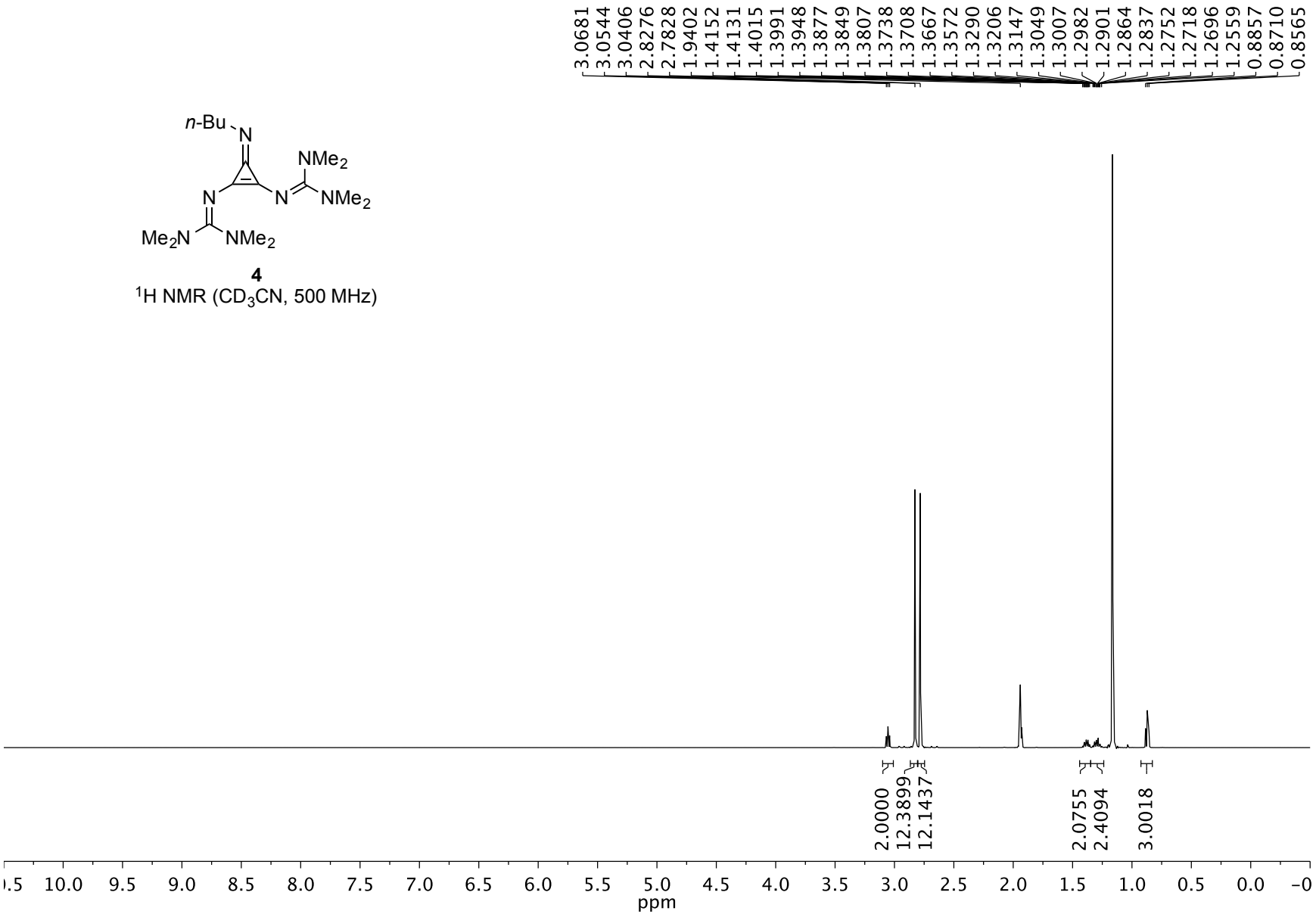


14•HBF$_4$ **P$_2$-Et**

^{1}H NMR (CD$_3$CN, 500 MHz)

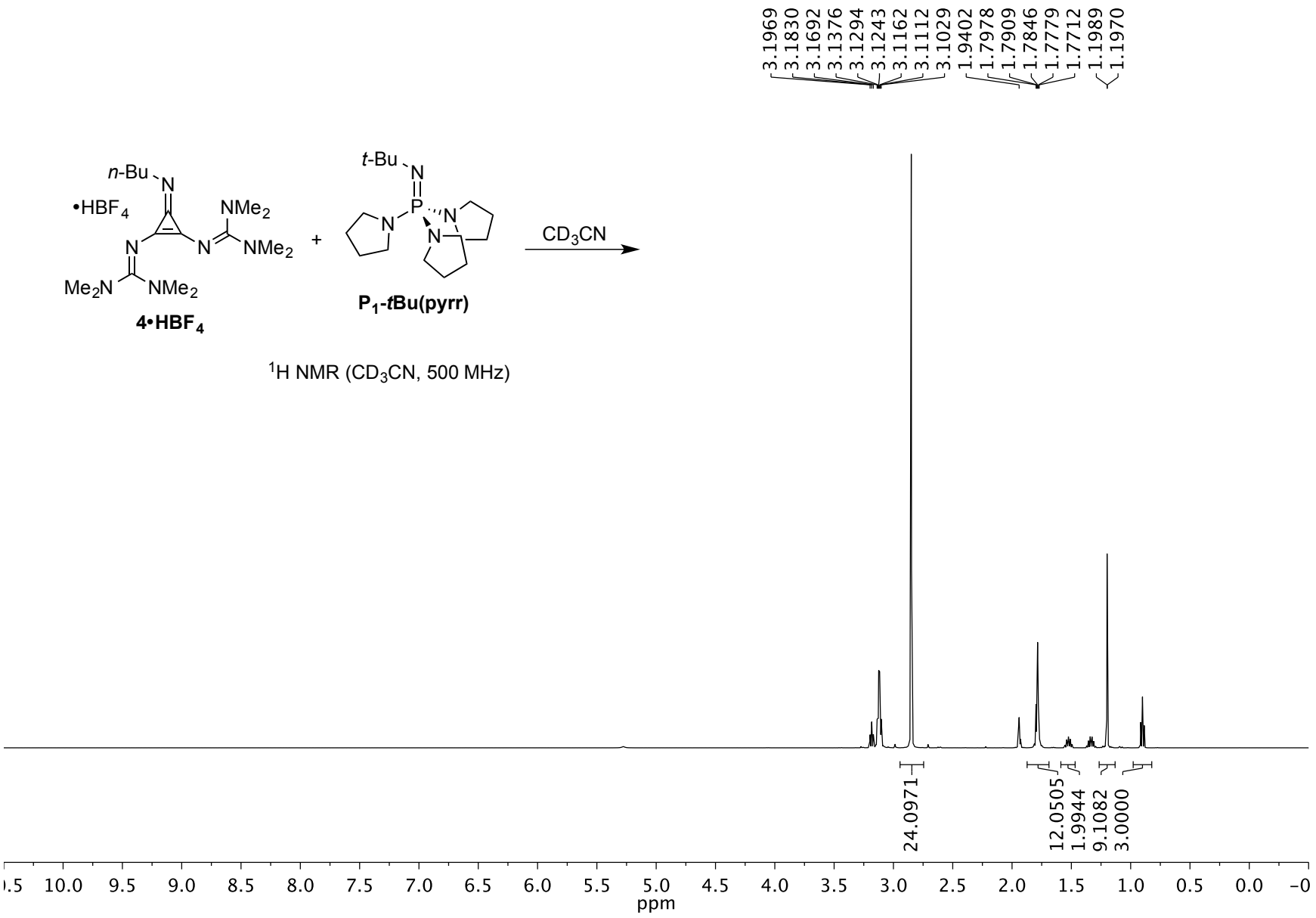


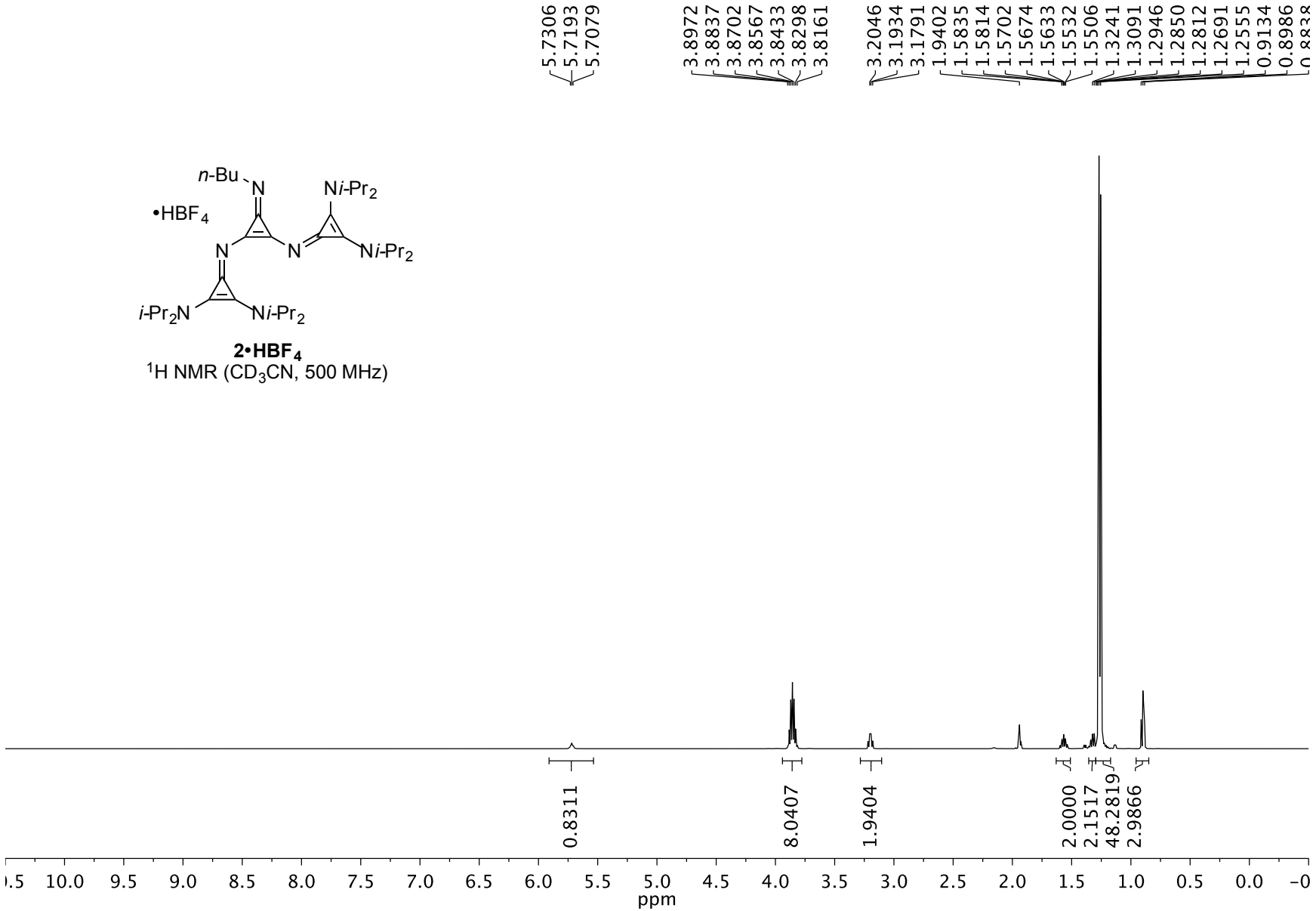

6.0658
3.2705
3.2568
3.2454
3.2318
2.8778
1.9402
1.6190
1.6051
1.6000
1.5929
1.5906
1.5866
1.5788
1.5752
1.5721
1.5613
1.3957
1.3848
1.3807
1.3698
1.3657
1.3628
1.3550
1.3506
1.3478
1.3403
1.3359
1.3212
0.9403
0.9256
0.9108
n-Bu
•HBF4
NMe2
NMe2
Me2N
NMe2
4•HBF4
1H NMR (CD3CN, 500 MHz)
0.9048
2.0000
24.0839
2.0020
2.0194
2.9987
ppm



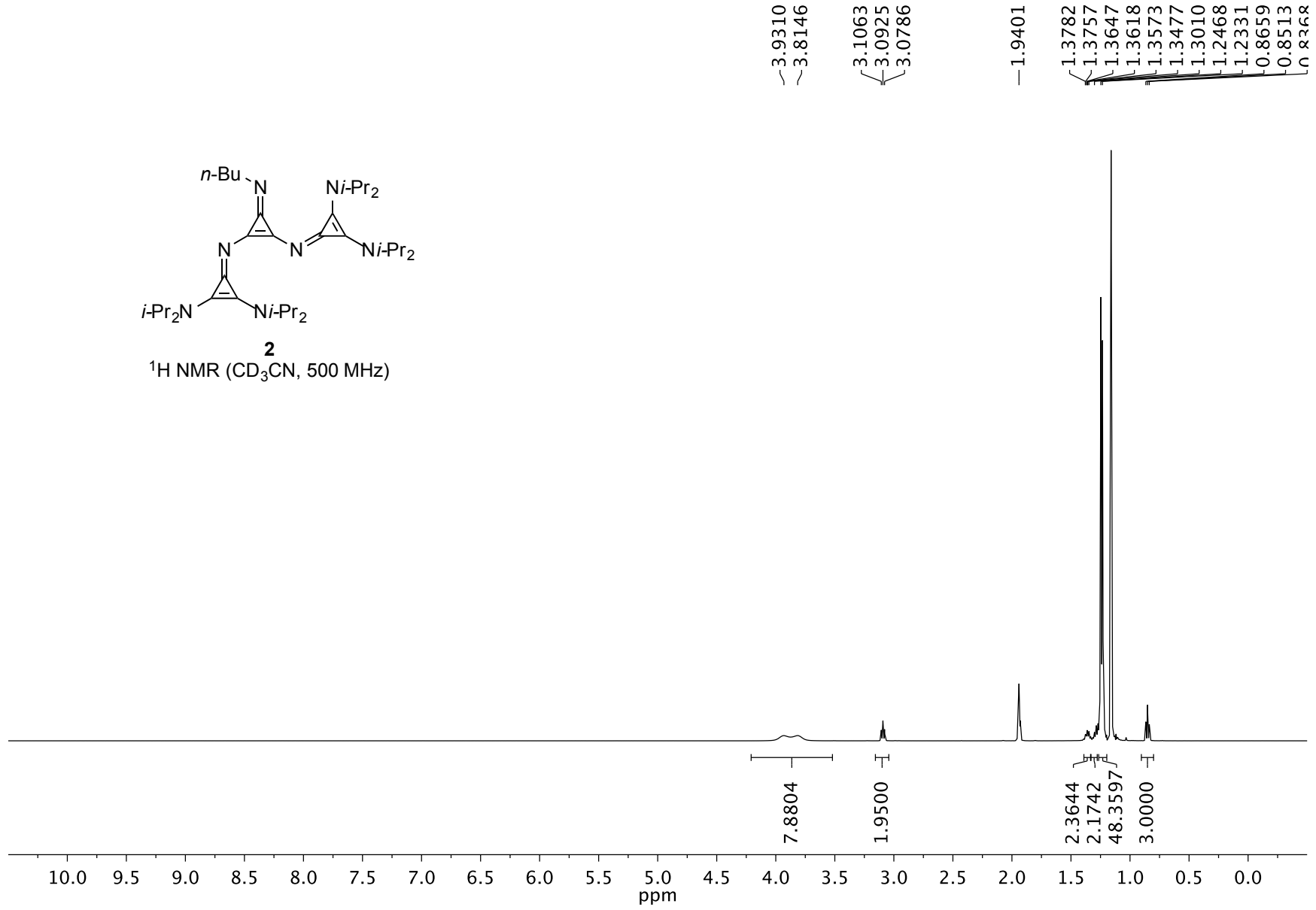
4

^{1}H NMR (CD_3CN, 500 MHz)


3.1969
3.1830
3.1692
3.1376
3.1294
3.1243
3.1162
3.1112
3.1029
1.9402
1.7978
1.7909
1.7846
1.7779
1.7712
1.1989
1.1970
n-Bu
•HBF4
NMe2
NMe2
N
N
N
Me2N
NMe2
4•HBF4
+
t-Bu
N
P
N
N
N
P1-tBu(pyrr)
CD3CN
1H NMR (CD3CN, 500 MHz)
24.0971
12.0505
1.9944
9.1082
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

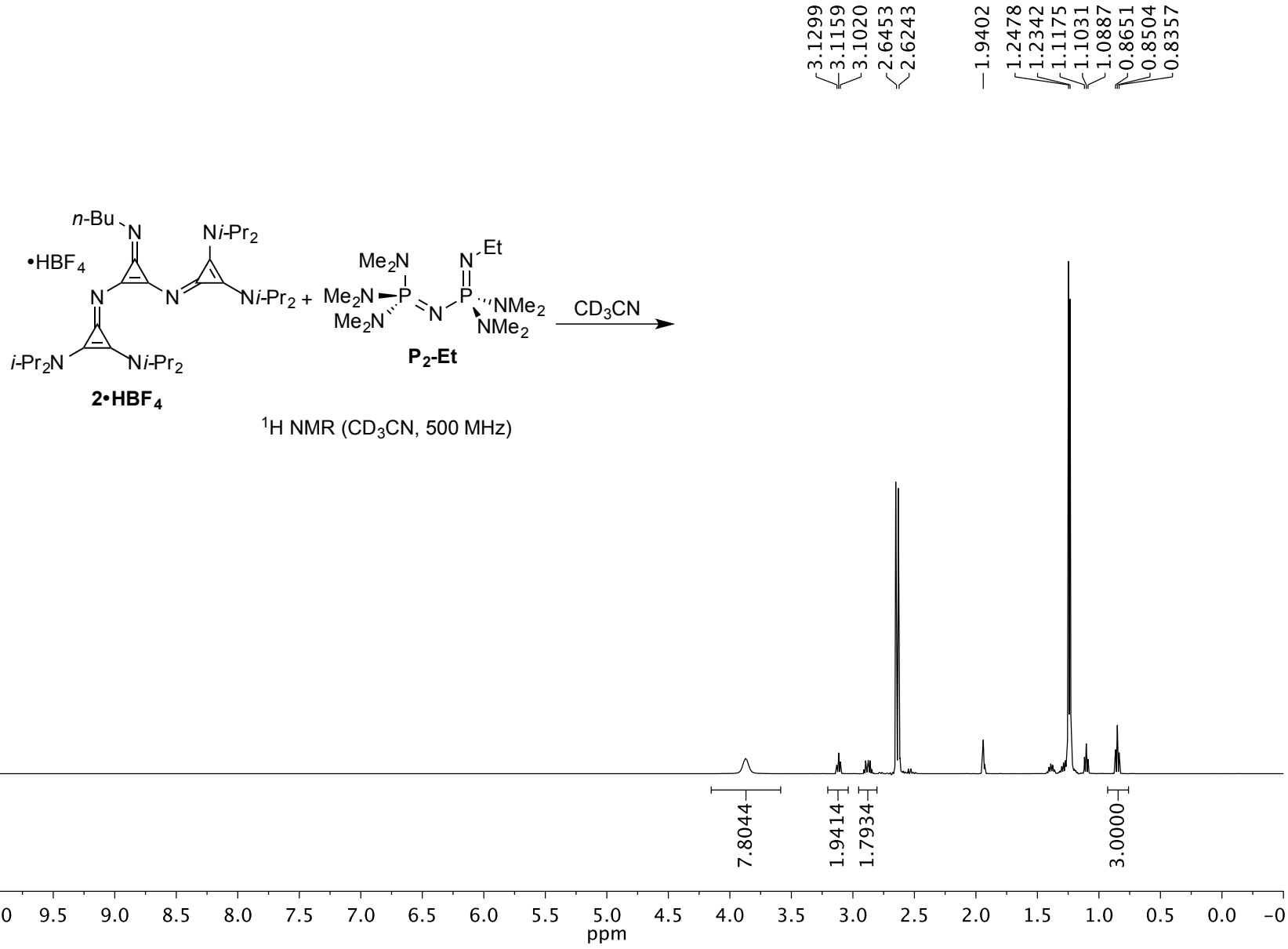


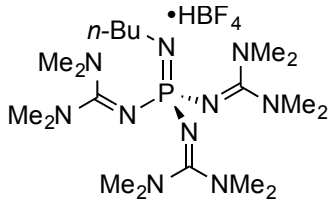
2•HBF$_4$
^{1}H NMR (CD_3CN, 500 MHz)



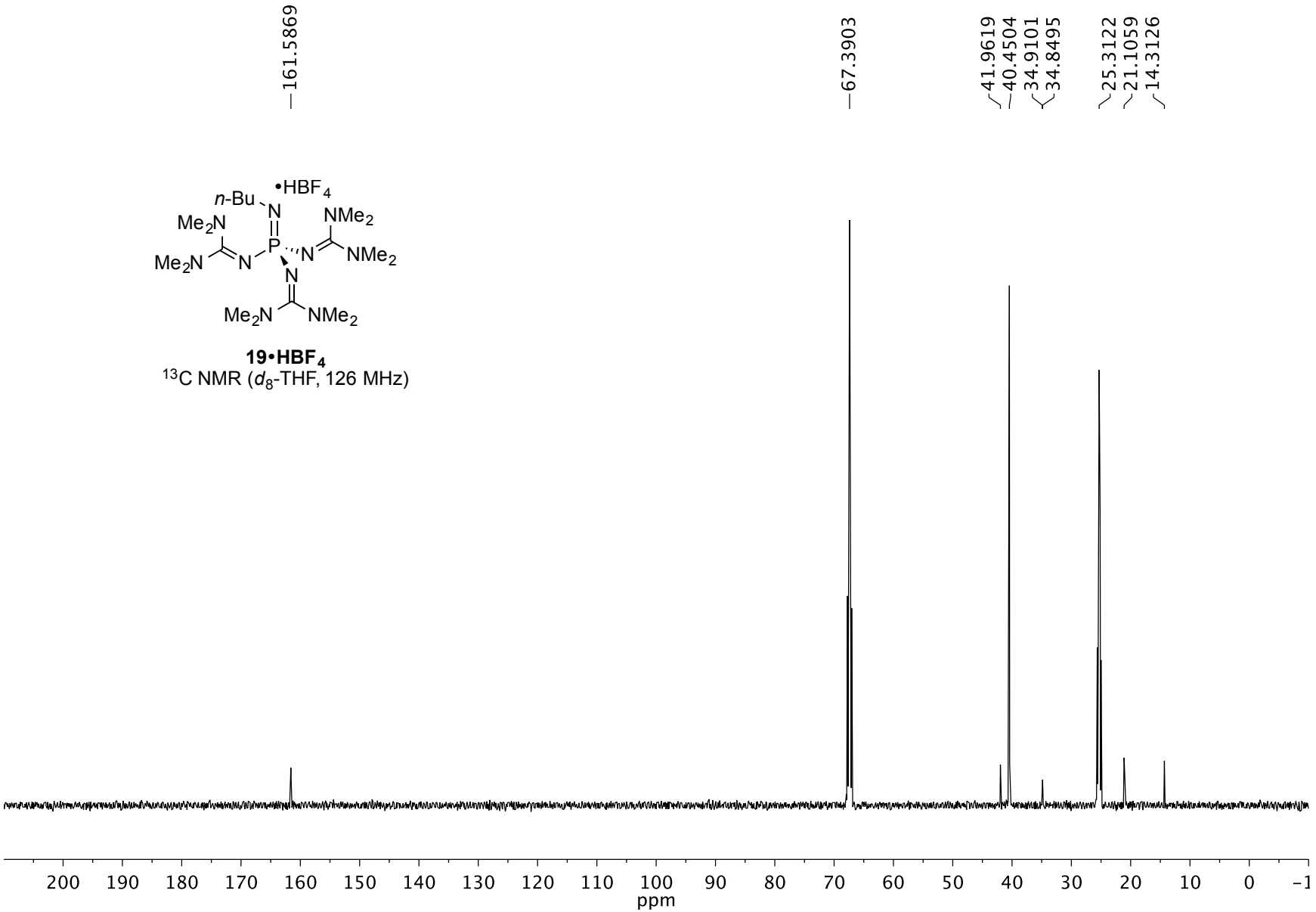
2

^{1}H NMR (CD_3CN, 500 MHz)

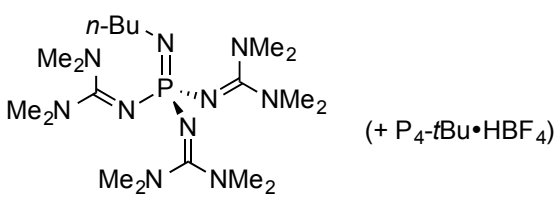

3.1299
3.1159
3.1020
2.6453
2.6243
1.9402
1.2478
1.2342
1.1175
1.1031
1.0887
0.8651
0.8504
0.8357
n-Bu
N
Ni-Pr2
•HBF4
N
N
Ni-Pr2 +
i-Pr2N
Ni-Pr2
2•HBF4
Me2N
N
Et
Me2N
P
N
P
NMe2
Me2N
NMe2
P2-Et
CD3CN
1H NMR (CD3CN, 500 MHz)
7.8044
1.9414
1.7934
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



19•HBF$_4$
^{1}H NMR (d_8-THF, 500 MHz)



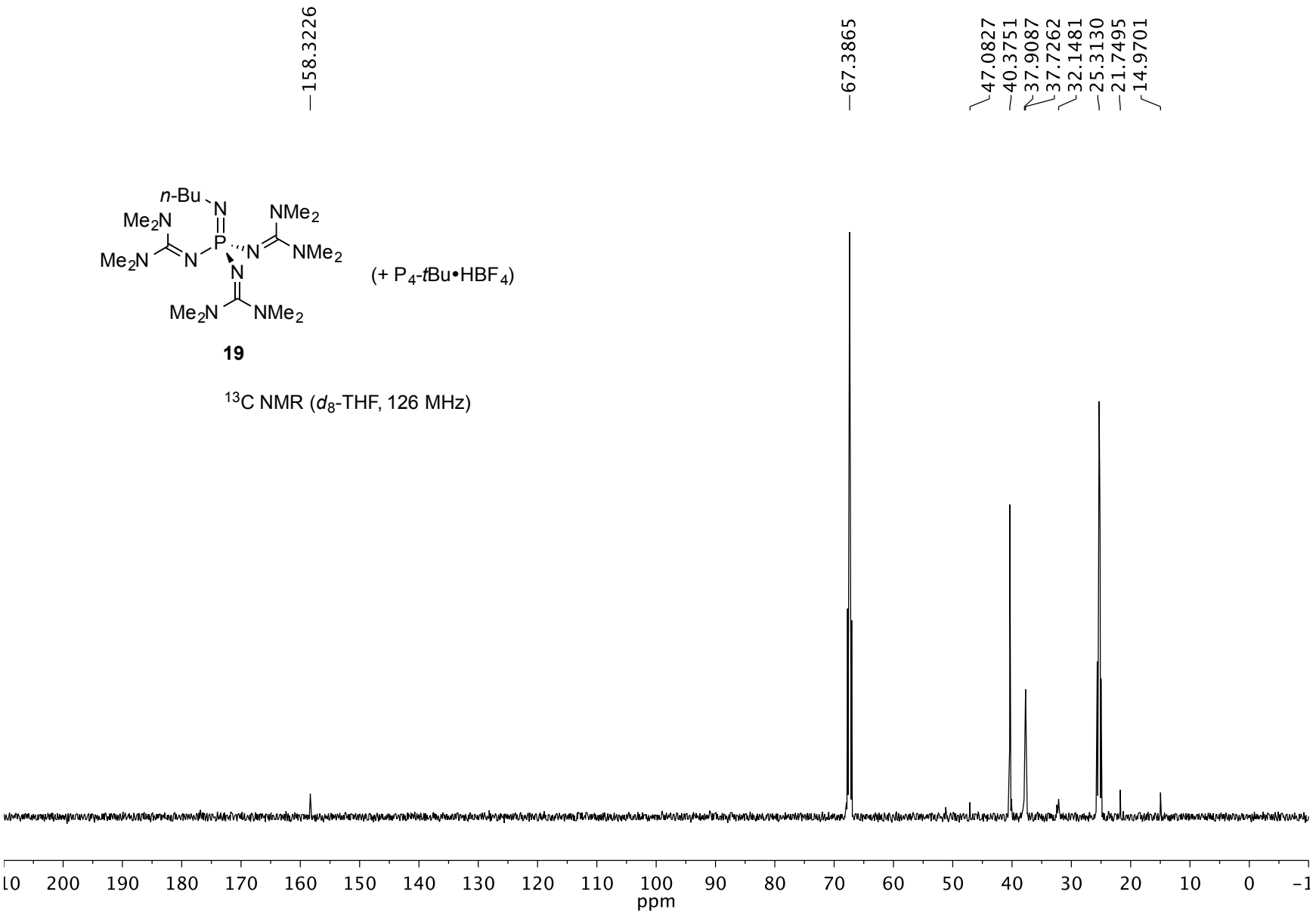
19•HBF$_4$
^{13}C NMR (d_8-THF, 126 MHz)

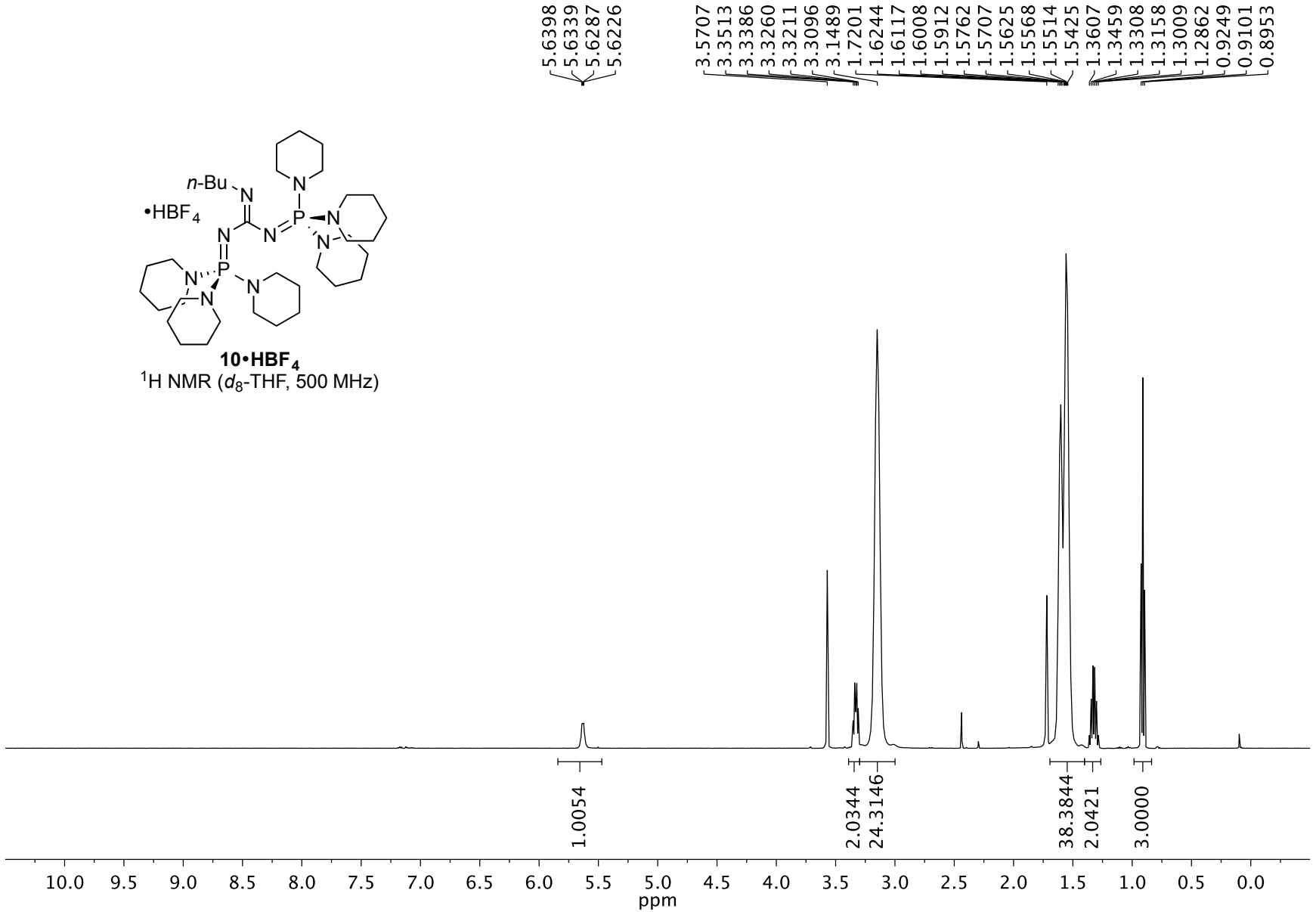


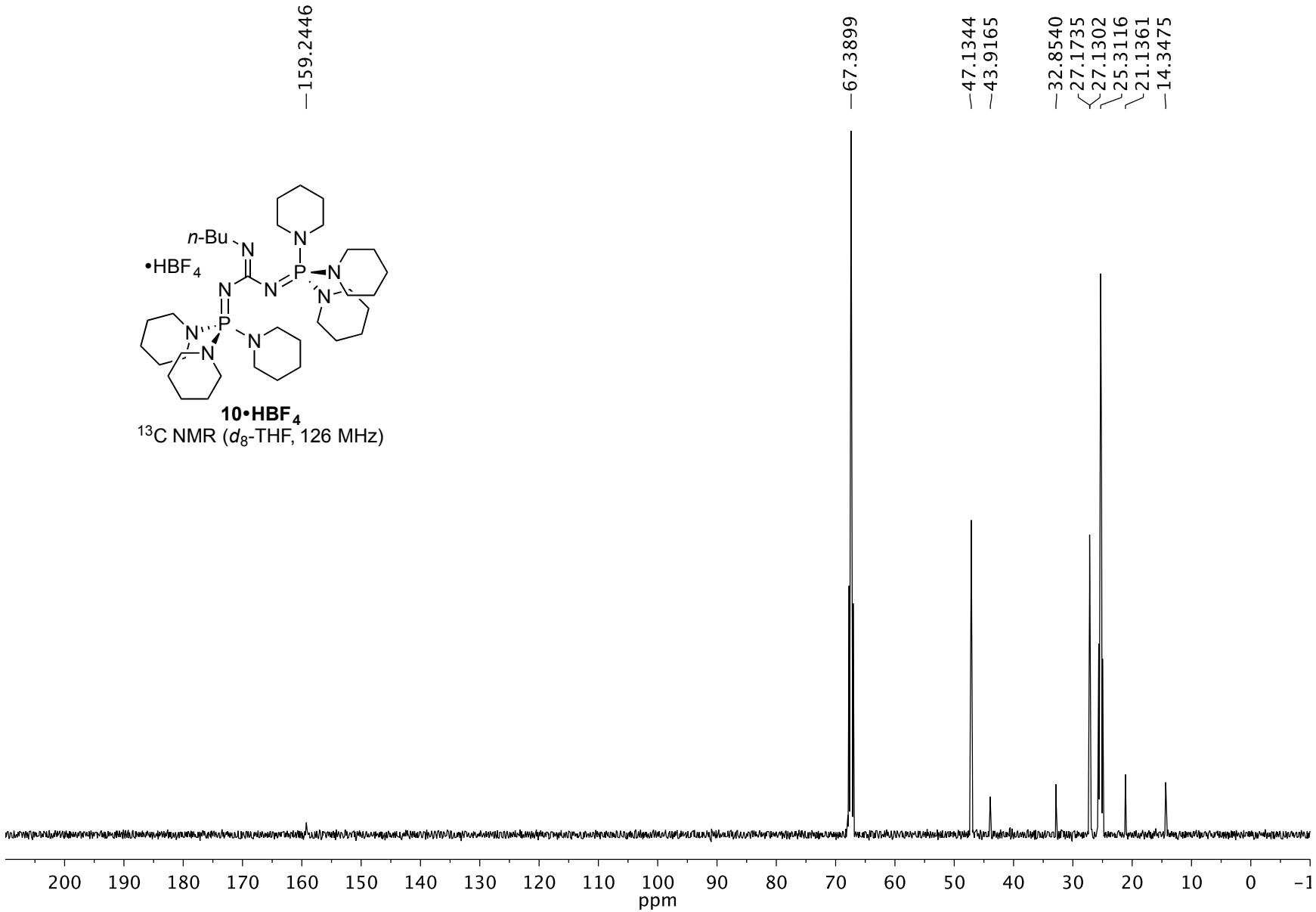
19

(+ P_4-*t*Bu•HBF_4)

^{1}H NMR (d_8-THF, 500 MHz)

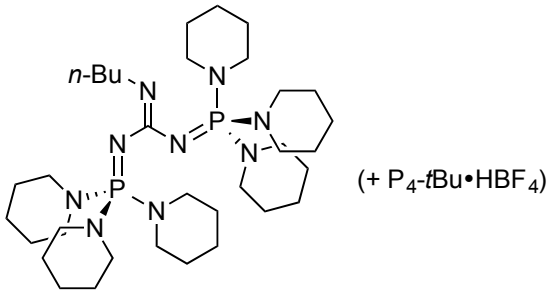

158.3226
67.3865
47.0827
40.3751
37.9087
37.7262
32.1481
25.3130
21.7495
14.9701
n-Bu
Me2N
NMe2
Me2N
N
P
N
NMe2
N
Me2N
NMe2
(+ P4-tBu•HBF4)
19
13C NMR (d8-THF, 126 MHz)
ppm


5.6398
5.6339
5.6287
5.6226
3.5707
3.3513
3.3386
3.3260
3.3211
3.3096
3.1489
1.7201
1.6244
1.6117
1.6008
1.5912
1.5762
1.5707
1.5625
1.5568
1.5514
1.5425
1.3607
1.3459
1.3308
1.3158
1.3009
1.2862
0.9249
0.9101
0.8953
n-Bu
•HBF4
10•HBF4
1H NMR (d8-THF, 500 MHz)
1.0054
2.0344
24.3146
38.3844
2.0421
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



10•HBF$_4$

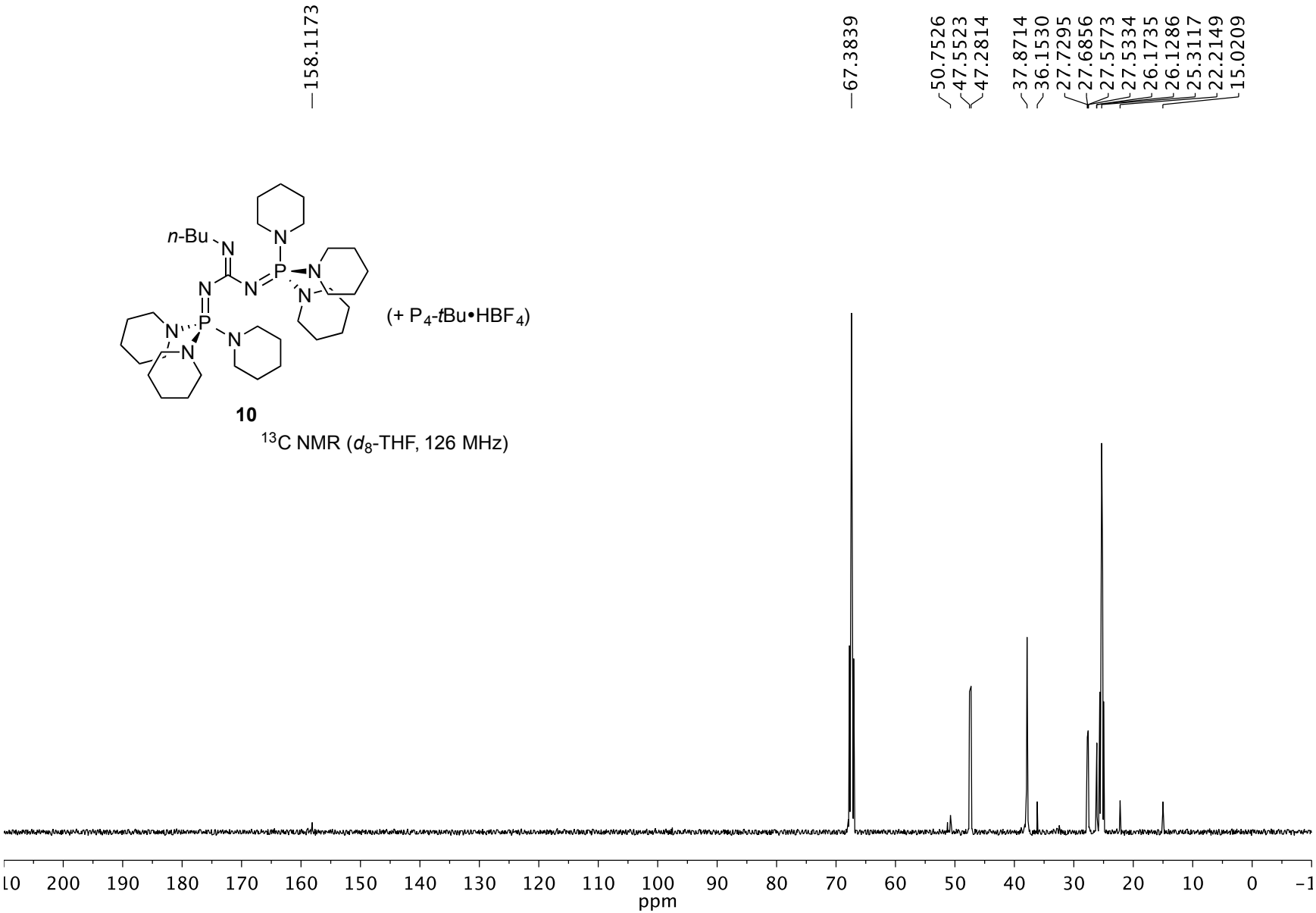
^{13}C NMR (d_8-THF, 126 MHz)

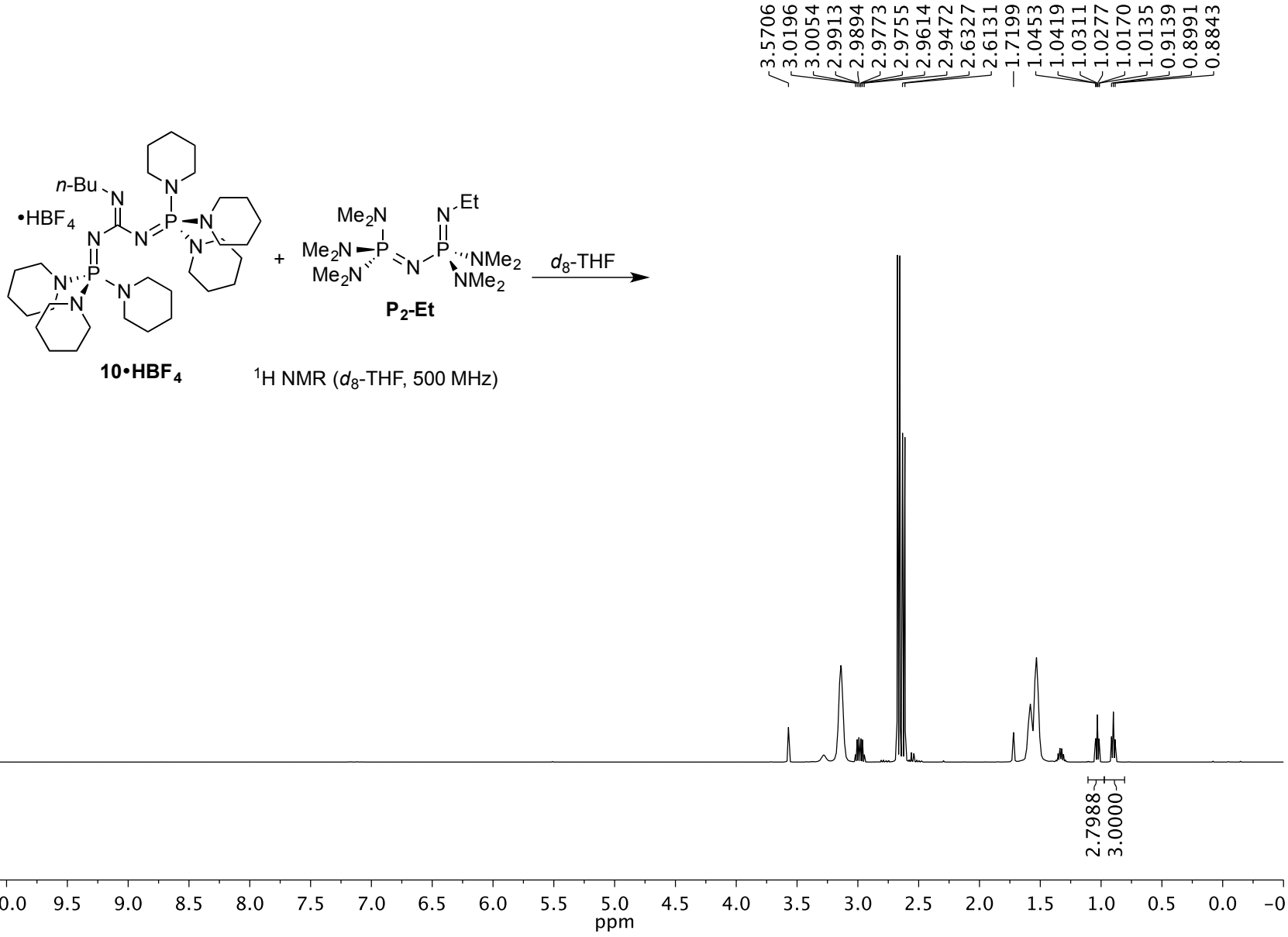


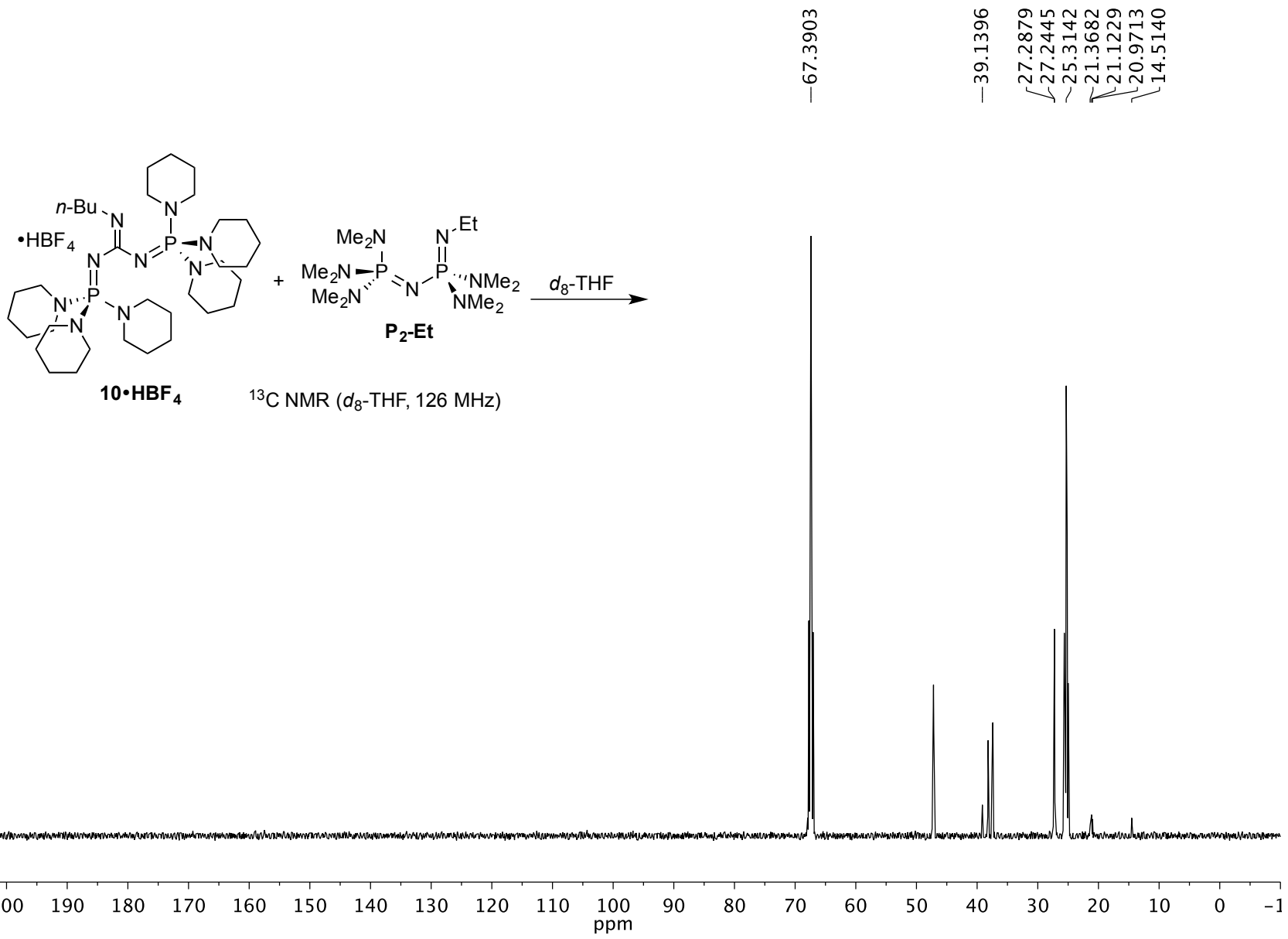
(+ P_4-*t*Bu•HBF_4)

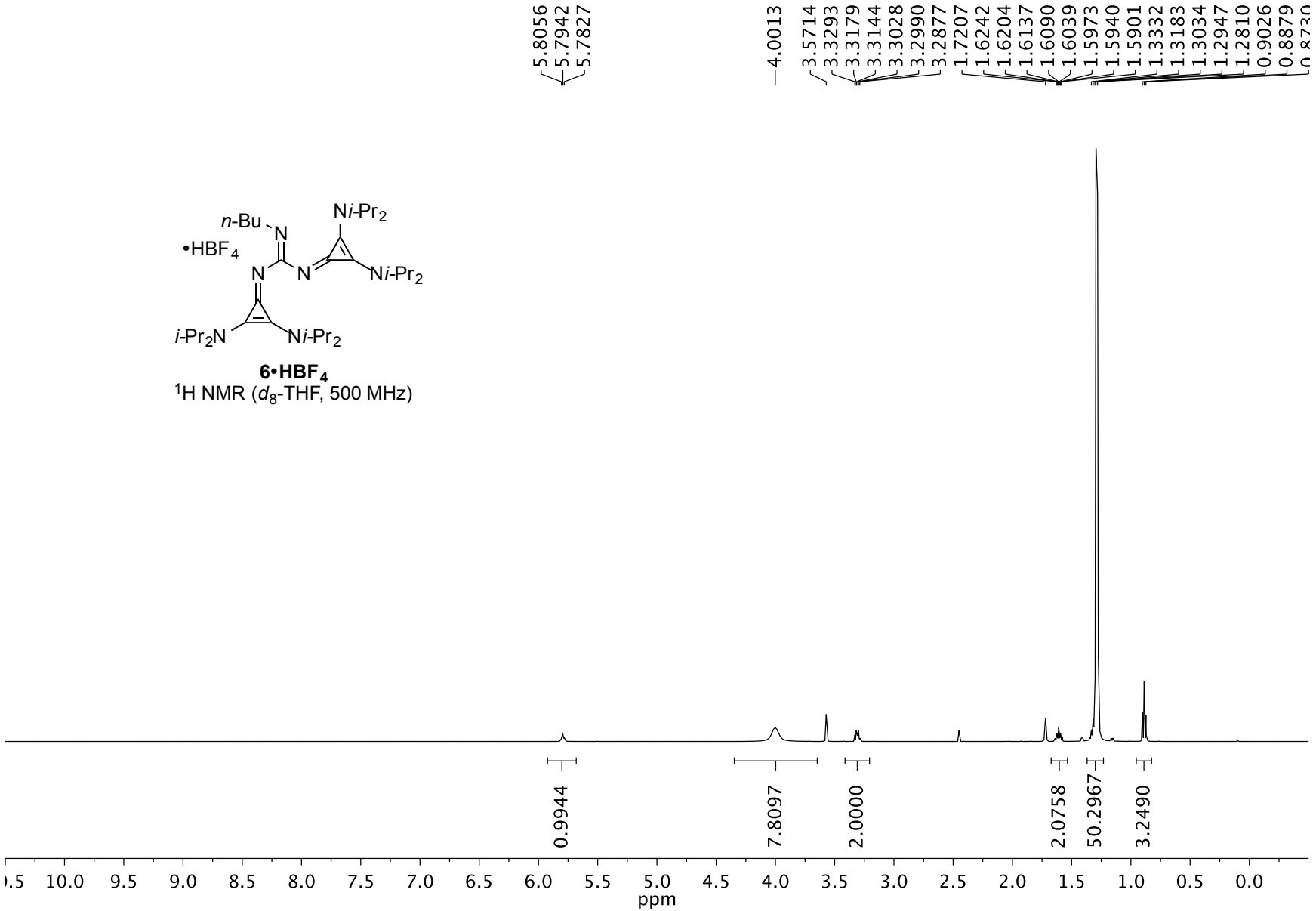
10

^{1}H NMR (d_8-THF, 500 MHz)

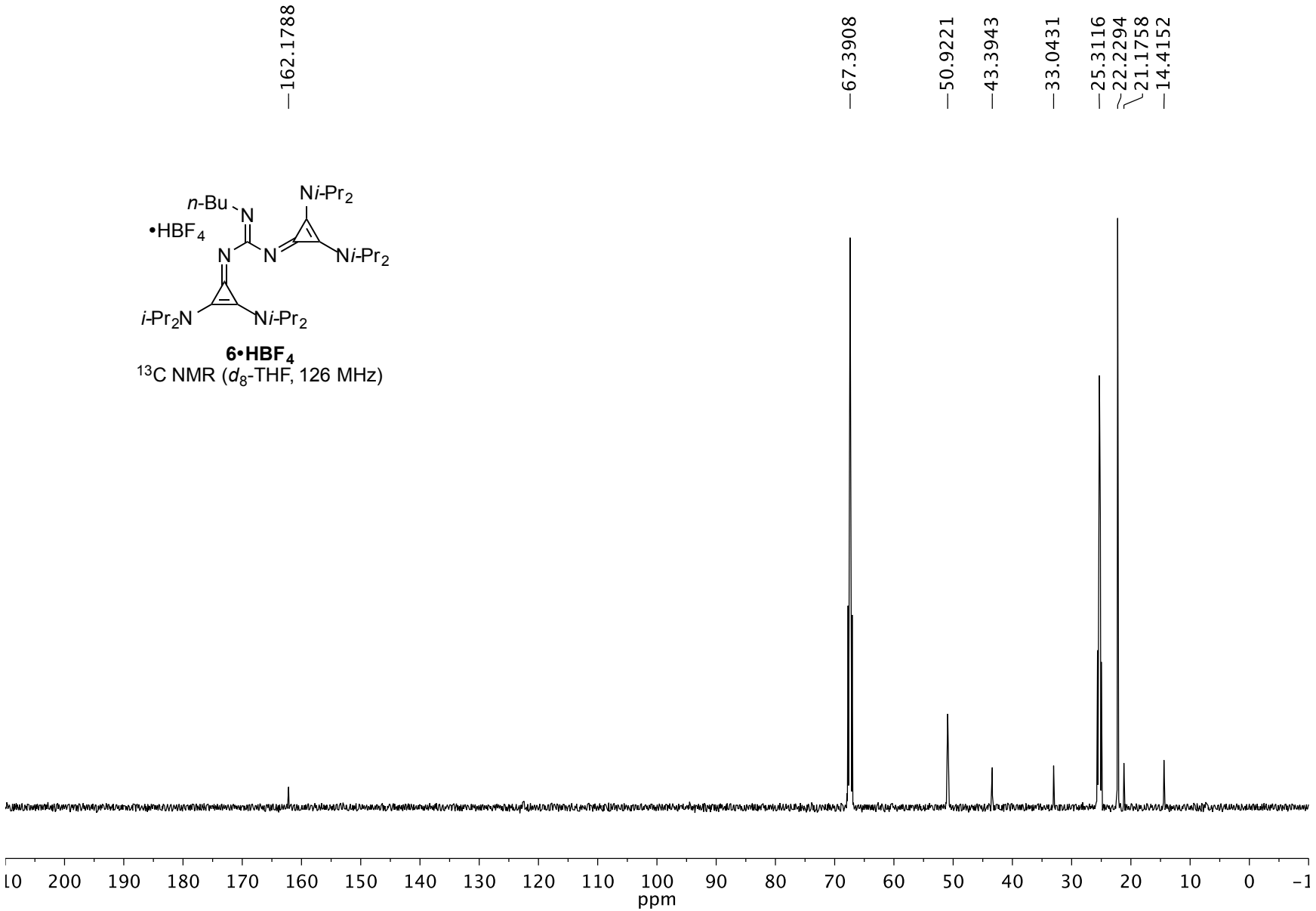

158.1173
67.3839
50.7526
47.5523
47.2814
37.8714
36.1530
27.7295
27.6856
27.5773
27.5334
26.1735
26.1286
25.3117
22.2149
15.0209
n-Bu
(+ P4-tBu•HBF4)
10
13C NMR (d8-THF, 126 MHz)
ppm


3.5706
3.0196
3.0054
2.9913
2.9894
2.9773
2.9755
2.9614
2.9472
2.6327
2.6131
1.7199
1.0453
1.0419
1.0311
1.0277
1.0170
1.0135
0.9139
0.8991
0.8843
n-Bu
•HBF4
Me2N
N
Et
Me2N
Me2N
P
N
P
NMe2
NMe2
d8-THF
P2-Et
10•HBF4
1H NMR (d8-THF, 500 MHz)
2.7988
3.0000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

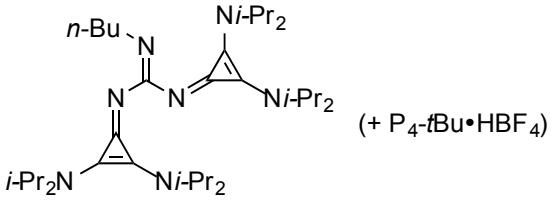

67.3903
39.1396
27.2879
27.2445
25.3142
21.3682
21.1229
20.9713
14.5140
n-Bu
•HBF4
Me2N
N
Et
Me2N
P
N
P
NMe2
Me2N
NMe2
d8-THF
P2-Et
10•HBF4
13C NMR (d8-THF, 126 MHz)
ppm



6•HBF$_4$
^{1}H NMR (d_8-THF, 500 MHz)



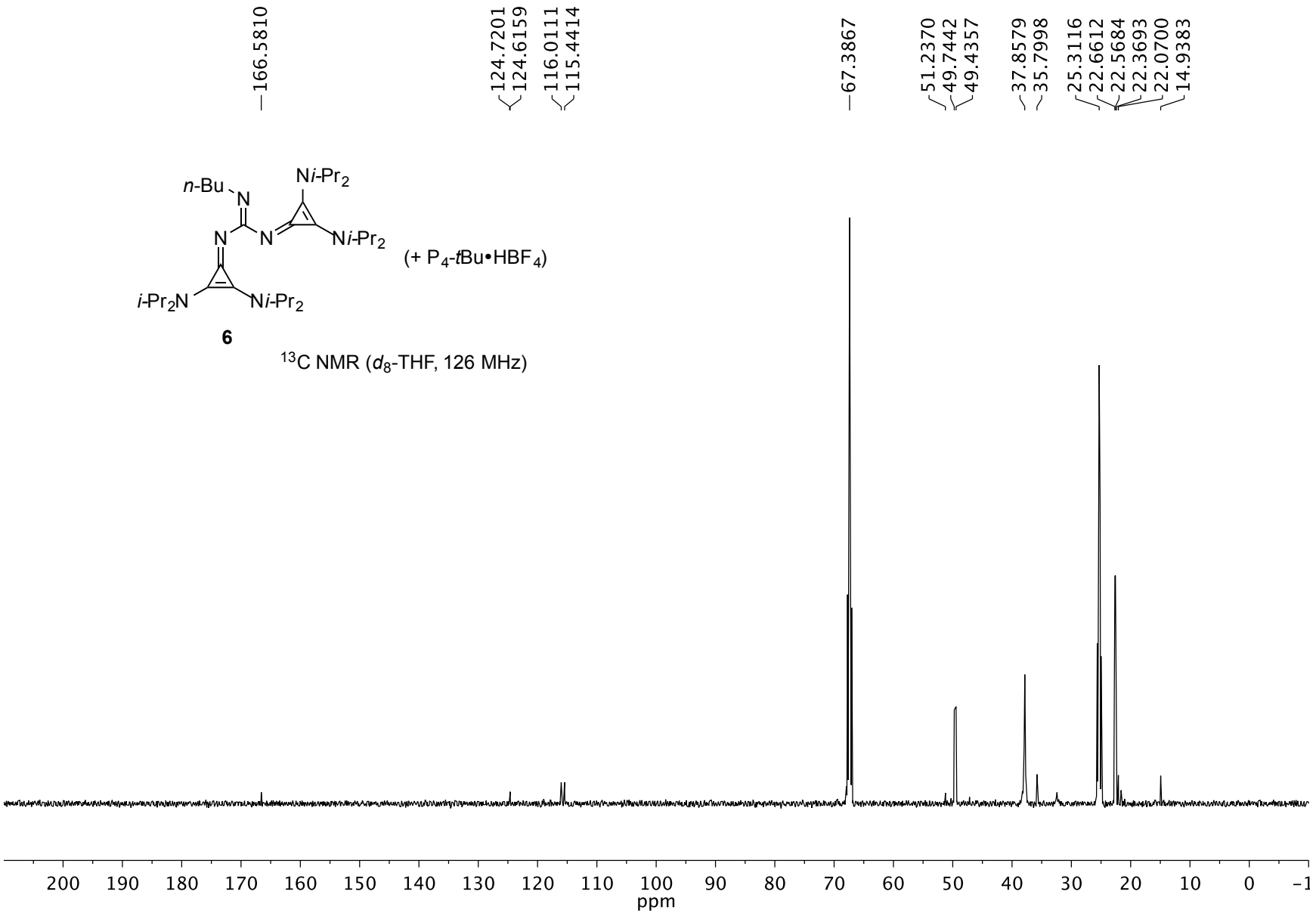
6•HBF$_4$
^{13}C NMR (d_8-THF, 126 MHz)

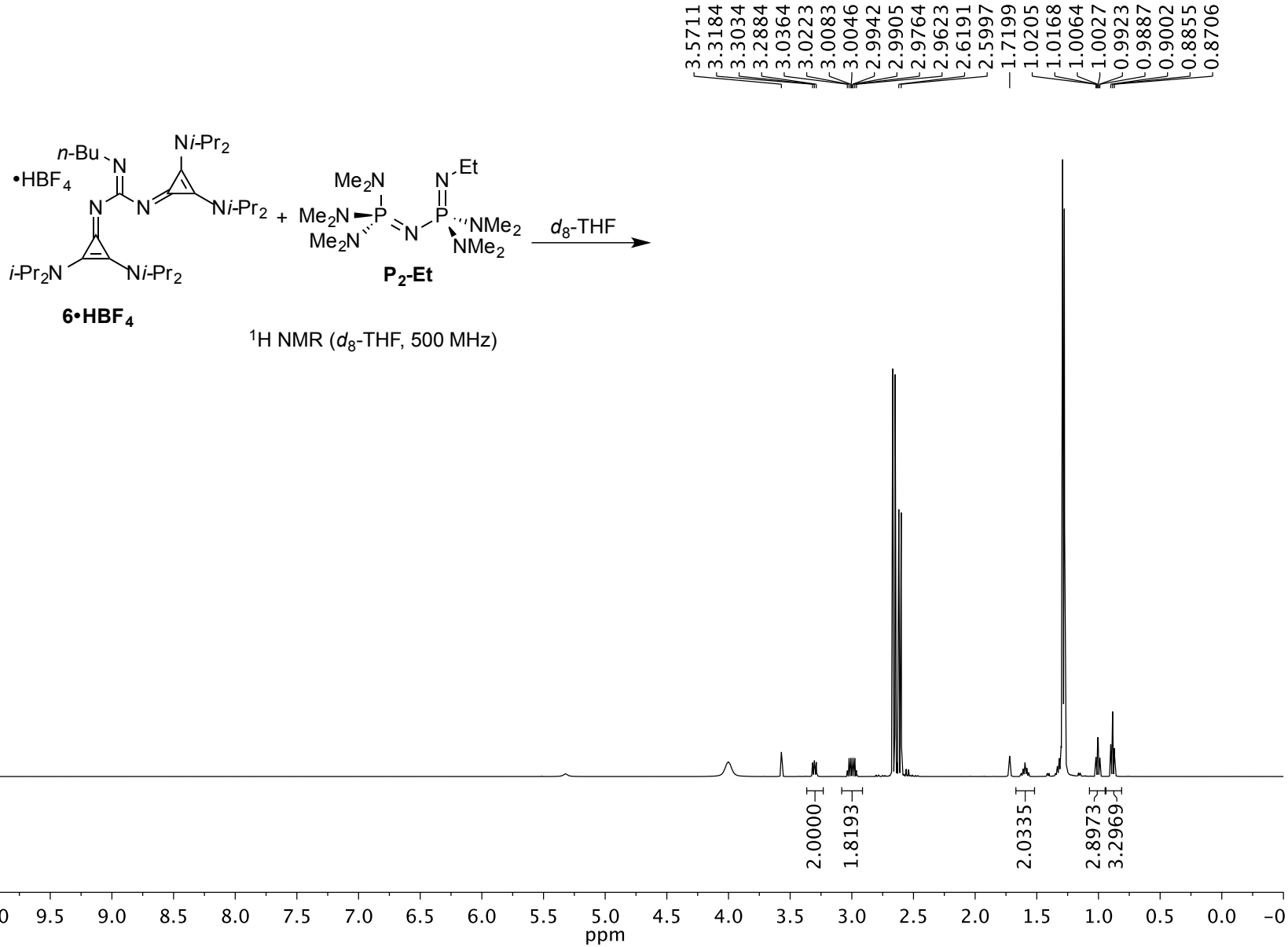


(+ P_4-*t*Bu•HBF_4)

6

^{1}H NMR (d_8-THF, 500 MHz)

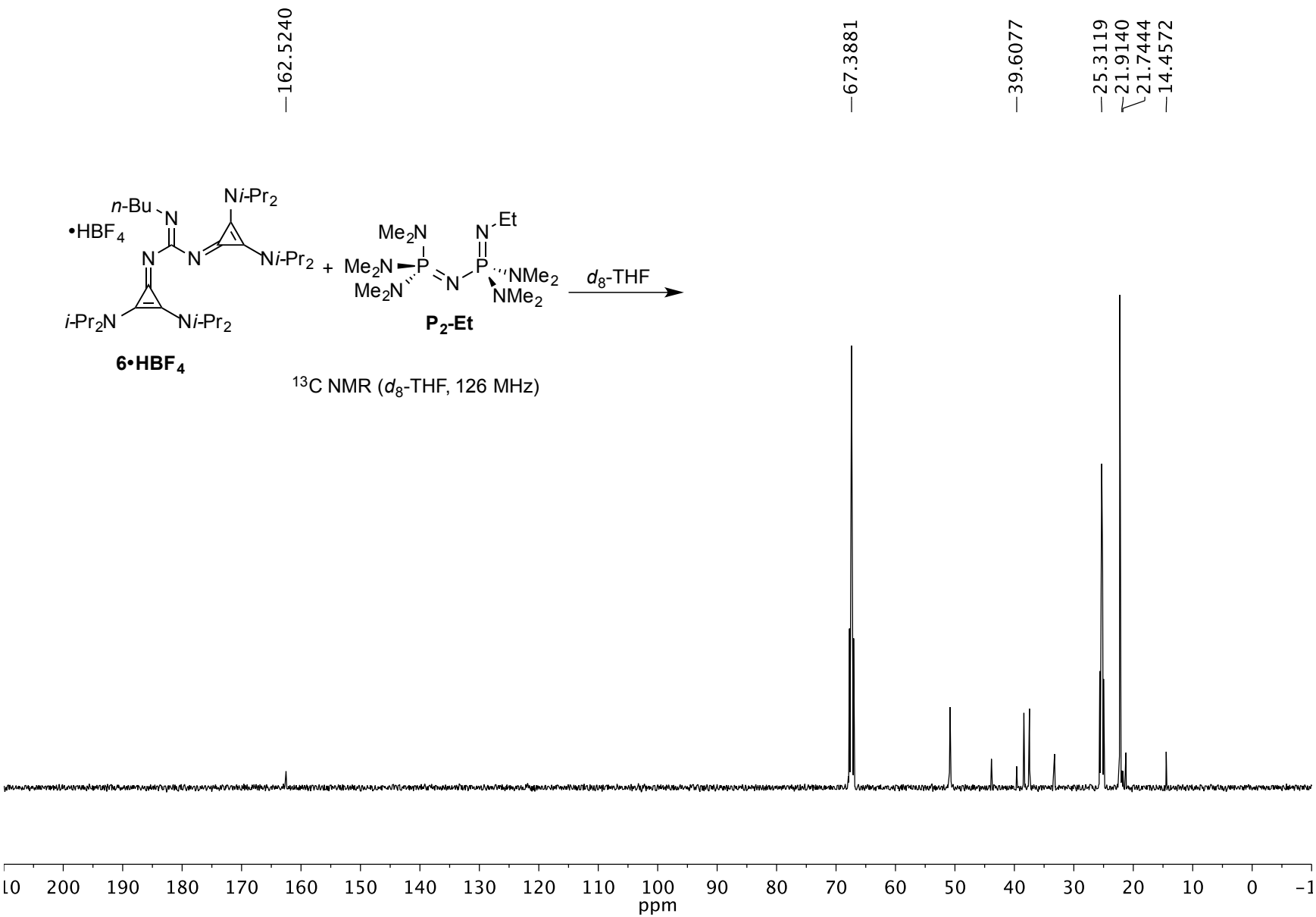

166.5810
124.7201
124.6159
116.0111
115.4414
67.3867
51.2370
49.7442
49.4357
37.8579
35.7998
25.3116
22.6612
22.5684
22.3693
22.0700
14.9383
n-Bu
N
N
N
N
Ni-Pr2
Ni-Pr2
i-Pr2N
Ni-Pr2
(+ P4-tBu•HBF4)
6
13C NMR (d8-THF, 126 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm



6•HBF$_4$

P$_2$-Et

^{1}H NMR (d_8-THF, 500 MHz)


162.5240
67.3881
39.6077
25.3119
21.9140
21.7444
14.4572
n-Bu
•HBF4
Ni-Pr2
Ni-Pr2
i-Pr2N
Ni-Pr2
6•HBF4
Me2N
Me2N
Me2N
N
Et
P
P
NMe2
NMe2
P2-Et
d8-THF
13C NMR (d8-THF, 126 MHz)
ppm